

VII. RESULTS OF CHEMICAL ANALYSES

A. Tenax Samples

As noted in Section VI, the PAH observed on the Tenax-GC cartridges are the most abundant and are generally gas-phase species. Naphthalene and the alkylnaphthalenes were the only PAH likely to be present mainly in the gas-phase which were on the recommended lists for monitoring. Not unexpectedly, GC/MS analysis of a Glendora Tenax sample in the full scanning mode (rather than the MID mode used for quantification) showed that, in addition to naphthalene and the methylnaphthalenes, several alkylbenzenes were also very abundant. Tenax cartridges with two flow rates (low-flow, $\sim 1 \text{ L min}^{-1}$; high-flow, $\sim 10 \text{ L min}^{-1}$) were utilized. This ensured that naphthalene could be quantified at the rural site (anticipated to have low ambient concentrations of PAH) and also allowed us to examine the less abundant PAH species. At Glendora each low-flow Tenax cartridge had a back-up cartridge to check for breakthrough. At all other sites back-up cartridges were generally used for four or five of the low-flow sampling periods. No significant ($<10\%$) breakthrough of naphthalene was observed on any of these back-up cartridges, indicating that naphthalene was collected quantitatively on the low-flow Tenax cartridges.

As a check of the integrity of the Tenax samples during storage, control Tenax cartridges were spiked with deuterated naphthalene, biphenyl, 1-nitronaphthalene, phenanthrene and anthracene ($\sim 10 \mu\text{g}$ each) in November 1986 and stored in the freezer. In April 1987 when the Glendora Tenax samples were analyzed, a control Tenax sample was removed from the freezer and analyzed along with the Glendora samples (see Section VI-A), with known amounts of the corresponding nondeuterated PAH being added prior to elution. The recovery of the deuterated standards was then calculated based upon the nondeuterated species added. This procedure was repeated with a second control Tenax in August 1987 when the Tenax from the six remaining sites were analyzed. No significant differences in the recoveries were observed for the two storage periods. The recoveries for the April and August analyses, respectively, were: naphthalene- d_8 (72%, 81%), biphenyl- d_{10} (73%, 66%), 1-nitronaphthalene- d_7 (67%, not analyzed), phenanthrene- d_{10} (83%, 82%), and anthracene- d_{10} (83%, 80%).

Tables VII-1 through VII-7 list the naphthalene concentrations measured during 12-hr day/night sampling intervals at the seven sites on the low-flow Tenax cartridges. The volume of each sample and the μg amounts of naphthalene for replicate GC/MS injections are given for the seven sites in Appendix C, Tables C-1 through C-7. As anticipated, the ambient concentrations of naphthalene were lowest at Pt. Arguello, ranging from ~40 to 200 ng m^{-3} . The highest naphthalene concentrations were observed at Glendora, where concentrations up to 6100 ng m^{-3} (1.1 ppb) were measured.

For Glendora, in addition to the low-flow Tenax samples, the full set of high-flow Tenax samples was analyzed. Table C-8 (from Final Report to ARB Contract No. A5-150-32) compares the concentrations of naphthalene and 1- and 2-methylnaphthalene measured on the low-flow and high-flow Tenax cartridges. The high-flow values for naphthalene were consistently lower than those obtained from the low-flow Tenax samples, indicating that naphthalene was not collected quantitatively at a sample flow rate of 10 L min^{-1} at the ambient temperatures encountered at Glendora. Therefore, we used the low-flow Tenax samples to quantify naphthalene at the six remaining sites in this study.

There was good agreement between the nighttime concentrations of the 1- and 2-methylnaphthalenes calculated from the low- and high-flow Tenax samples at Glendora (Table C-8). For the daytime samples when the observed concentrations were generally low, the high-flow values tended to be higher than the low-flow values and were judged to be somewhat more accurate. The low-flow back-up Tenax showed a significant signal interfering with the 1-methylnaphthalene quantification. This interference has been subtracted from the values given in Table C-8. However, because of this interference and the lower concentrations of methylnaphthalenes observed at the remaining six sites, the low-flow Tenax data for the methylnaphthalenes are not reported here.

Table VII-8 gives the concentrations of eight volatile PAH measured on the high-flow Tenax cartridges, and Table C-9 gives the corresponding μg values for replicate injections and the total sample volumes. As discussed above, all eighteen high-flow samples from Glendora were analyzed. Since the naphthalene data for the six additional sites were obtained from the low-flow Tenax samples, only a single day and a single

Table VII-1. Naphthalene Concentrations (ng m^{-3}) Measured at Glendora, CA, August 1986 (Day, 0800-2000 PDT; Night, 2000-0800 PDT)

Date		ng m^{-3} ^{a,b}
8/12/86	Day	2,200
8/12-13/86	Night	5,000
8/13/86	Day	2,400
8/13-14/86	Night	4,800
8/14/86	Day	2,500
8/14-15/86	Night	3,000
8/15/86	Day	2,800
8/15-16/86	Night	4,100
8/16/86	Day	3,200
8/16-17/86	Night	3,400
8/17/86	Day	2,000
8/17-18/86	Night	4,300
8/18/86	Day	4,100
8/18-19/86	Night	4,200
8/19/86	Day	4,300
8/19-20/86	Night	3,800
8/20/86	Day	4,100
8/20-21/86	Night	6,100

^aAverage of replicate injections.

^bSampled at $\sim 1 \text{ L min}^{-1}$ onto Tenax GC cartridges.

Table VII-2. Naphthalene Concentrations (ng m^{-3}) Measured at Yuba City, CA, October 1986 (Day, 0700-1900 PDT; Night, 1900-0700 PDT)

Date		ng m^{-3} ^{a,b}
10/16/86	Day	230
10/16-17/86	Night	66
10/17/86	Day ^c	90
10/18/86	Day	170
10/18-19/86	Night	74
10/20/86	Day ^c	54
10/20-21/86	Night	680
10/21/86	Day	1,100
10/21-22/86	Night	2,400
10/23/86	Day ^c	290
10/23-24/86	Night ^c	110
10/25/86	Day ^c	200

^aAverage of replicate injections.

^bSampled at $\sim 1 \text{ L min}^{-1}$ onto Tenax-GC cartridges.

^cLess than 12-hr sampling period, see Appendix B, Table B-2 for details.

Table VII-3. Naphthalene Concentrations (ng m^{-3}) Measured at Concord, CA, December 1986 and January 1987 (Day, 0500-1700 PST; Night, 1700-0500 PST)

Date		ng m^{-3} ^{a,b}
12/6-7/86	Night ^c	4,600
12/7/86	Day	870
12/7-8/86	Night	3,000
12/8/86	Day	1,300
12/8-9/86	Night	2,400
12/9/86	Day	1,000
12/10-11/86	Night	1,800
12/12/86	Day	610
1/13/87	Day ^c	470
1/13-14/87	Night ^c	1,400
1/14/87	Day	1,100
1/14-15/87	Night	440
1/17-18/87	Night	2,800
1/18/87	Day	990
1/18-19/87	Night	1,600
1/19/87	Day	1,200
1/21/87	Day	590
1/21-22/87	Night	2,300
1/22/87	Day ^c	910

^aAverage of replicate injections.

^bSampled at $\sim 1 \text{ L min}^{-1}$ onto Tenax-GC cartridges.

^cLess than 12-hr sampling period, see Appendix B, Table B-3 for details.

Table VII-4. Naphthalene Concentrations (ng m^{-3}) Measured at Mammoth Lakes, CA, February 1987 (Day, 0500-1700 PST; Night, 1700-0500 PST)

Date		ng m^{-3} ^{a,b}
2/14/87	Day	1,400
2/14-15/87	Night ^c	780
2/15-16/87	Night	850
2/16/87	Day	560
2/16-17/87	Night	1,400
2/17/87	Day	500
2/17-18/87	Night	880
2/18/87	Day ^c	570
2/20-21/87	Night	1,400
2/21/87	Day	590
2/21-22/87	Night	420
2/22/87	Day	480
2/22-23/87	Night	130
2/25-26/87	Night ^c	290
2/26/87	Day	580
2/27-28/87	Night	990
2/28/87	Day	830
2/28-3/1/87	Night	1,500

^aAverage of replicate injections.

^bSampled at -1 l min^{-1} onto Tenax-GC cartridges.

^cLess than 12-hr sampling period, see Appendix B, Table B-4 for details.

Table VII-5. Naphthalene Concentrations (ng m^{-3}) Measured at Oildale, CA, March and April 1987 (Day, 0600-1800 PST; Night, 1800-0600 PST)

Date		ng m^{-3} ^{a,b}
3/29-30/87	Night	260
3/30/87	Day	120
3/31/87	Day ^c	330
3/31-4/1/87	Night	370
4/1/87	Day	220
4/1-2/87	Night	330
4/2/87	Day	250
4/7/87	Day	210
4/7-8/87	Night	440
4/8/87	Day	260
4/8-9/87	Night	500
4/9/87	Day	260
4/9-10/87	Night	410
4/10/87	Day	260
4/10-11/87	Night	280

^aAverage of replicate injections.

^bSampled at $\sim 1 \text{ L min}^{-1}$ onto Tenax-GC cartridges.

^cLess than 12-hr sampling period, see Appendix B, Table B-5 for details.

Table VII-6. Naphthalene Concentrations (ng m^{-3}) Measured at Reseda, CA, May and June 1987 (Day, 0700-1900 PDT; Night, 1900-0700 PDT)

Date		ng m^{-3} ^{a,b}
5/27-28/87 ^c	Night	1,000
5/28/87	Day	520
5/28-29/87	Night	1,300
5/29/87	Day	750
5/29-30/87	Night	1,400
5/30/87 ^d	Day	370
5/31/87	Day	410
5/31-6/1/87	Night	1,600
6/1/87	Day	340
6/1-2/87	Night	1,600
6/2/87	Day	650
6/2-3/87	Night	990
6/13-14/87	Night	710
6/14/87	Day	350
6/14-15/87	Night	350
6/15/87	Day	450

^aAverage of replicate injections.

^bSampled at $\sim 1 \text{ L min}^{-1}$ onto Tenax-GC cartridges.

^cLess than 12-hr sampling period, see Appendix B, Table B-6 for details.

^dMissing 5/30-31/87 Night; no internal standard added.

Table VII-7. Naphthalene Concentrations (ng m^{-3}) Measured at Pt. Arguello, CA, July 1987 (Day, 0700-1900 PDT; Night, 1900-0700 PDT)

Date		ng m^{-3} ^a
7/4/87	Day	52
7/4-5/87	Night	110
7/5/87	Day	49
7/5-6/87	Night	60
7/6/87	Day	57
7/6-7/87	Night	150
7/7/87	Day	75
7/7-8/87	Night	b
7/8/87	Day	62
7/8-9/87	Night	97
7/9/87	Day	86
7/9-10/87	Night	83
7/10/87	Day	150
7/10-11/87	Night	200
7/11/87	Day	59
7/11-12/87	Night	b
7/12/87	Day	89
7/12-13/87	Night	120
7/13/87	Day	86
7/13-14/87	Night	41

^aSampled at $\sim 1 \text{ L min}^{-1}$ onto Tenax-GC cartridges.

^bFlow not maintained throughout sample.

Table VII-8. Concentrations of Volatile PAH (ng m^{-3}) Measured for Selected Day/Night Intervals^a at the Seven Sampling Sites in California. Samples were collected onto High-Flow Tenax-GC Solid Adsorbent Cartridges

Location and Date		ng m^{-3} b								
		Naphthalene ^c	1-Methyl-naphthalene	2-Methylnaphthalene	Biphenyl	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	
Glendora	Day	^d (2,200) ^e	170 ^e	250 ^e	^d	^d	^d	^d	^d	^d
Glendora	Night	2,200 (5,000) ^e	500	900	220	39	32	49	64	
Glendora	Day	1,100 (2,400) ^e	160	320	95	~3	4	30	26	
Glendora	Night	1,900 (4,800) ^e	390	730	170	12	22	37	51	
Glendora	Day	820 (2,500) ^e	130	260	70	~3	4	30	20	
Glendora	Night	1,600 (3,000) ^e	330	640	100	23	17	34	40	
Glendora	Day	^d (2,800) ^e	170 ^e	190 ^e	^d	^d	^d	^d	^d	
Glendora	Night	2,000 (4,100) ^e	380	730	66	10	21	35	42	
Glendora	Day	690 (3,200) ^e	98	200	52	~3	~4	23	16	
Glendora	Night	1,800 (3,400) ^e	350	700	98	~3	24	40	37	
Glendora	Day	470 (2,000) ^e	76	170	36	~3	~5	27	20	

(continued)

Table VII-8 (continued) - 2

Location and Date		ng m ⁻³ b								
		Naphthalene ^c	1-Methylnaphthalene	2-Methylnaphthalene	Biphenyl	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	
Glendora	8/17-18/86	Night	1,800 (4,300) ^e	330	680	54	4	30	47	51
Glendora	8/18/86	Day	670 (4,100) ^e	120	260	43	~3	5	31	26
Glendora	8/18-19/86	Night	1,600 (4,200) ^e	280	570	67	~3	28	43	46
Glendora	8/19/86	Day	500 (4,300) ^e	90	200	36	~3	4	23	21
Glendora	8/19-20/86	Night	1,600 (3,800) ^e	290	600	60	~3	28	44	50
Glendora	8/20/86	Day	810 (4,100) ^e	150	320	53	~3	6	33	29
Glendora	8/20-21/86	Night	_d (6,100) ^e	510 ^e	870 ^e	_d	_d	_d	_d	_d
Yuba City	10/21/86	Day	1,500 (1,100) ^e	300	680	26	5	3	20	21
Yuba City	10/21-22/86	Night	2,000 (2,400) ^e	510	1,000	28	29	22	31	35
Concord	12/6-7/86	Night	2,000 (4,600) ^e	370	780	84	110	29	52	79
Concord	12/7/86	Day	570 (870) ^e	84	190	2	1 ^f	2	13	13
Mammoth Lakes	2/20-21/87	Night	1,800 (1,400) ^e	210	340	95	7	19	75	230

Table VII-8 (continued) - 3

Location and Date	ng m ⁻³ b							
	Naphthalene ^c	1-Methylnaphthalene	2-Methylnaphthalene	Biphenyl	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene
Mammoth Lakes 2/21/87 Day	940 (590) ^e	120	240	12	2	3 ^f	24	65
Oildale 4/7/87 Day	290 (210) ^e	36	72	10	8	8	8	2
Oildale 4/7-8/87 Night	690 (440) ^e	160	310	21	5	9	23	14
Reseda 5/28-29/87 Night	1,700 (1,300) ^e	350	750	17	18	8	21	22
Reseda 5/29/87 Day	990 (750) ^e	160	330	25	8	8	14	12
Pt. Arguello 7/6-7/87 Night	39 (150) ^e	8	8	8	8	8	8	8
Pt. Arguello 7/7/87 Day	43 (75) ^e	8	8	8	8	8	8	8

^aSee Tables VII-1 through VII-7 for the 12-hr day and 12-hr night sampling intervals at each site.

^bAverage of replicate GC/MS injections.

^cNaphthalene was not always collected quantitatively on the high-flow Tenax as can be seen from comparing these values with those of the low-flow Tenax samples given in parentheses.

^dNo high-flow Tenax sample.

^eLow-flow Tenax values.

^fSingle quantification.

^gLevels too low to quantify.

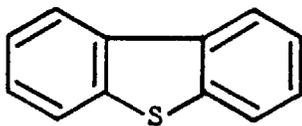
night were analyzed of the high-flow Tenax samples collected at these sites. The day/night pair chosen for analysis at each site included one of the highest naphthalene concentrations at that site (as determined from the low-flow Tenax samples).

As discussed above, the naphthalene data from the low-flow Tenax should be quantitative, but some breakthrough of naphthalene may occur on the high-flow Tenax. In Table VII-8 the low-flow Tenax naphthalene values are given beneath those of the high-flow. The two values either agree reasonably well (breakthrough on the high-flow Tenax being controlled by temperature and the adsorption capacity of the Tenax), or the low-flow values are greater. Since at Glendora (where both the highest temperatures and concentrations were encountered) the methylnaphthalene values from the low-flow and high-flow Tenax agree, the high-flow methylnaphthalene values for the remaining sites should also be quantitative. The additional PAH listed in Table VII-8 are less volatile than the methylnaphthalenes, and no breakthrough of these would be expected.

From Table VII-8 it can be seen that naphthalene was always the most abundant species, followed by 2-methylnaphthalene and then 1-methylnaphthalene. Acenaphthylene was unusually high in the Concord evening sample analyzed. The data set obtained from the Tenax samples collected at Glendora shows significant day/night variations in the PAH concentrations which, as discussed in Section X, show the importance of atmospheric reactions of gas-phase PAH.

B. PUF Plug Samples

PAH Sampled on PUF Plugs. GC/MS analysis in the scanning mode of the PAH-containing HPLC fraction (see Section VI-B for details) of a Glendora PUF plug sample extract showed this fraction to contain fluorene, phenanthrene, anthracene, fluoranthene, pyrene, the sulfur-containing dibenzothiophene (structure below),



as well as several alkyl-PAH (these being at lower concentrations than their corresponding parent PAH). It must be remembered that the PAH are distributed between the gaseous and particle phases in ambient air and that the quantities measured on the PUF plugs are the sum of the PAH present in the gas phase and the PAH initially present on the POM but "blown-off" during the collection period.

A control PUF plug was spiked as described above for the Tenax controls. After storage in the freezer from November, 1986 to August, 1987, the following recoveries were obtained: naphthalene-d₈, 62%; biphenyl-d₁₀, 65%; 1-nitronaphthalene-d₇, 72%; phenanthrene-d₁₀, 84%; anthracene-d₁₀, 79%. The most volatile species quantified on the PUF plugs was 1-nitronaphthalene and, therefore, freezer storage of the PUF plugs was adequate.

As described in Section V, twenty-four PUF plug sample composites were made for analysis. At the Glendora sampling site four (rather than the three used elsewhere) PUF plugs were used in the modified Hi-vols. Two additional samples from Glendora, comprised of the fourth PUF plugs from Samples #3 and #4, were analyzed to measure breakthrough from the first three PUF plugs. The most abundant PAH collected on the PUF plugs were generally phenanthrene and fluorene. It can be seen from Appendix Table C-10 (which is taken from the Final Report to ARB Contract No. A5-150-32) that a large fraction of the fluorene was found on the fourth PUF plugs, indicating that fluorene was not collected quantitatively by three or even four PUF plugs at the ambient temperatures encountered at Glendora. The lack of significant quantities of dibenzothiophene, phenanthrene, anthracene, fluoranthene, and pyrene on the fourth PUF plug (Appendix Table C-10) indicates that these species were quantitatively collected on three PUF plugs at Glendora (some fluoranthene and pyrene were also present on the particles collected on the filters). For the remaining six sites, therefore, only three PUF plugs in series were used.

Table VII-9 gives the concentrations of the PAH observed on the PUF plugs (summing the quantities on the three or four PUF plugs) for the twenty-four composite samples obtained from the seven sites in California, and Table C-11 lists the volumes sampled and the µg quantities measured for replicate GC/MS injections. The values given for fluorene should, as

Table VII-9. PAH Concentrations Measured for Single or Composited Day/Night Sampling Intervals on PUF Plugs (ng m⁻³) at the Seven Sampling Sites in California

Location and Dates ^a	ng m ⁻³ b,c						
	Fluorene ^d	Dibenzo- thiophene	Phenan- threne	Anthra- cene	Fluor- anthene ^e	Pyrene ^e	
Glendora 8/13/86	Sample #1 Day	7.7	2.6	16.1	0.48	4.0	2.5
Glendora 8/13-14/86	Sample #2 Night	17.5	3.3	23.2	1.9	6.2	5.5
Glendora 8/15, 16, 17, 18/86	Sample #3 Day	9.8	2.6	15.9	0.31	4.2	2.4
Glendora 8/15-16, 16-17, 17-18, 18-19/86	Sample #4 Night	25.7	3.1	22.4	1.2	5.2	4.1
Glendora 8/20/86	Sample #5 Day	6.2	2.7	19.0	0.54	5.9	3.6
Glendora 8/20-21/86	Sample #6 Night	20.8	4.5	31.8	1.8	6.8	4.9
Yuba City 10/16, 18, 20/86	Sample #1 Day	5.5	2.4	10.6	0.72	3.2	2.0
Yuba City 10/17, 23/86	Sample #2 Day	3.7	1.1	6.6	0.31	2.0	1.1
Yuba City 10/16-17, 18-19, 20-21, 23-24/86	Sample #3 Night	4.2	1.1	5.3	0.53	1.7	1.3
Concord 12/8, 9/86; 1/19/87	Sample #1 Day	9.2	2.2	18.0	3.3	7.6	7.6

(continued)

Table VII-9 (continued) - 2

Location and Dates ^a		ng m ⁻³ b,c						
		Fluorene ^d	Dibenzo- thiophene	Phenan- threne	Anthra- cene	Fluor- anthene ^e	Pyrene ^e	
Concord 1/18,21,22/87	Sample #2 Day	10.7	1.6	17.4	1.8	6.3	5.1	
Concord 12/6-7,7-8,8-9/86	Sample #3 Night	21.4	2.7	41.2	13.1	17.8	15.8	
Concord 1/17-18,18-19,21-22/87	Sample #4 Night	34.3	4.1	66.4	17.0	25.2	20.3	
Concord 12/10-11/86; 1/14-15/87	Sample #5 Night	11.4	2.6	20.5	4.0	6.7	6.4	
Mammoth Lakes 2/14,16,17,21,22,26,28/87	Sample #1 Day	9.8	1.0	21.7	6.0	9.3	8.3	
Mammoth Lakes 2/16-17,17-18,20-21,27-28; 2/28-3/1/87	Sample #2 Night	26.5	0.65	60.4	21.2	15.8	12.2	
Mammoth Lakes 2/14-15,15-16,21-22,22-23,25-26/87	Sample #3 Night	8.5	0.41	19.5	5.3	4.1	3.4	
Oildale 3/30,31/87; 4/1,2,7,8,9,10/87	Sample #1 Day	1.2	0.81	6.0	0.51	1.3	1.3	
Oildale 3/29-30/87; 4/9-10,10-11/87	Sample #2 Night	5.2	1.1	8.5	0.66	1.2	1.2	
Oildale 3/31-4/1/87; 4/1-2,7-8,8-9/87	Sample #3 Night	6.6	1.6	11.8	0.98	1.6	1.6	
Reseda 5/28,29,30,31/87; 6/1,2,14,15/87	Sample #1 Day	2.7	1.6	14.7	1.2	4.3	3.2	

(continued)

Table VII-9 (continued) - 3

Location and Dates ^a		ng m ⁻³ b,c					
		Fluorene ^d	Dibenzo- thiophene	Phenan- threne	Anthra- cene	Fluor- anthene ^e	Pyrene ^e
Reseda	Sample #2 Night	9.5	1.7	17.9	2.0	4.1	3.5
5/27-28,28-29,29-30,30-31,5/31-6/1; 6/1-2,2-3,13-14,14-15/87							
Pt. Arguello	Sample #1 Day	0.56	0.20	1.8	0.13	0.11	0.09
7/4,5,6,7,8,9,10,11,12/87							
Pt. Arguello	Sample #2 Night	1.7	0.43	4.1	0.23	0.20	0.14
7/4-5,5-6,6-7,7-8,8-9,9-10,10-11,11-12/87							

^aSee Section V for full details of compositing.

^bAverage of 2 or 3 injections.

^cFour PUF plugs in series were used at Glendora, three PUF plugs were used at all other sites.

^dLower limit due to breakthrough.

^eSome present on the particles as well.

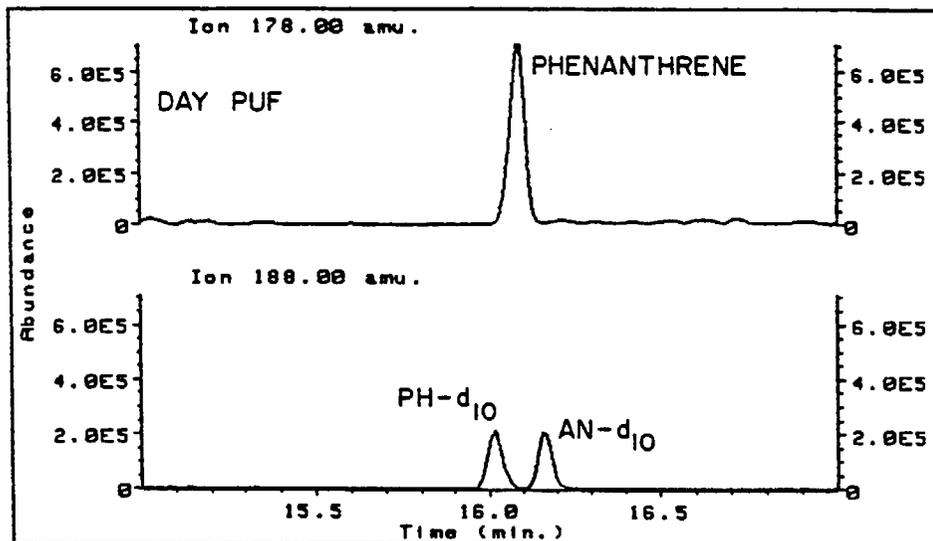
discussed above, be considered a lower limit to the ambient concentrations due to the possibility of breakthrough.

At the Glendora sampling site, the volatile PAH were generally more abundant during the nighttime than daytime sampling intervals. These diurnal variations were attributed (Final Report to ARB Contract No. A5-150-32; see also Sections IX and X below) both to meteorological conditions and to atmospheric reactions of the PAH. Different relative abundances of isomeric PAH showed the importance of atmospheric reactions. Thus, as illustrated in Figure VII-1, which shows the GC/MS/MID traces from the analysis of Glendora PUF plug Samples #1 (day) and #2 (night) for the isomeric PAH phenanthrene and anthracene, a higher ratio of anthracene/phenanthrene was observed in the evening samples, consistent with anthracene being more readily removed by reaction with the OH radical during daylight hours than phenanthrene. Similarly, the GC/MS/MID traces of Glendora PUF plug Samples #1 and #2 for the analyses of the isomeric PAH of M.W. 202 (Figure VII-2), show that acephenanthrylene, an isomer of fluoranthene and pyrene expected to be more reactive than these PAH towards ozone (Atkinson and Aschmann 1988) was generally not observed in the daytime PUF plug samples from Glendora. It should be noted that the identification of acephenanthrylene is based on retention time matching of the m/z 202 molecular ion peak with that of an authentic standard.

The highest ratios of acephenanthrylene/pyrene (or acephenanthrylene/fluoranthene) observed on PUF plugs were at Concord. Figure VII-3 shows the GC/MS/MID analyses of Concord Samples #2 (days) and #4 (nights) for the M.W. 202 species. Again, as at Glendora, the evening sample had the higher ratio of acephenanthrylene/pyrene. At this industrial site, however, varying day/night emissions patterns, as well as differing reactivities of the M.W. 202 species, may have contributed to the observed day/night differences in relative abundances.

Nitroarenes Sampled on PUF Plugs. The HPLC fractions of the PUF plug extracts eluting from 22 to 34 min (Section VI-B and Figure VI-1) contained the volatile nitroarene species. The most abundant volatile nitroarenes were 1- and 2-nitronaphthalene. GC/MS analysis in the full scanning mode of a Glendora sample showed that this nitroarene-containing HPLC fraction also contained alkyl nitrophenols.

GLENDORA, CA 8/13/86 0800-2000HR



GLENDORA, CA 8/13-14/86 2000-0800HR

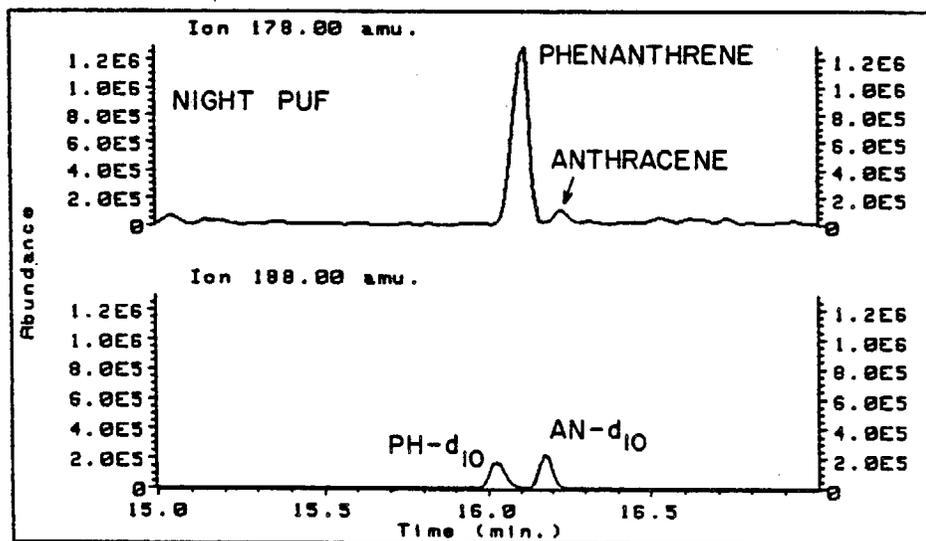
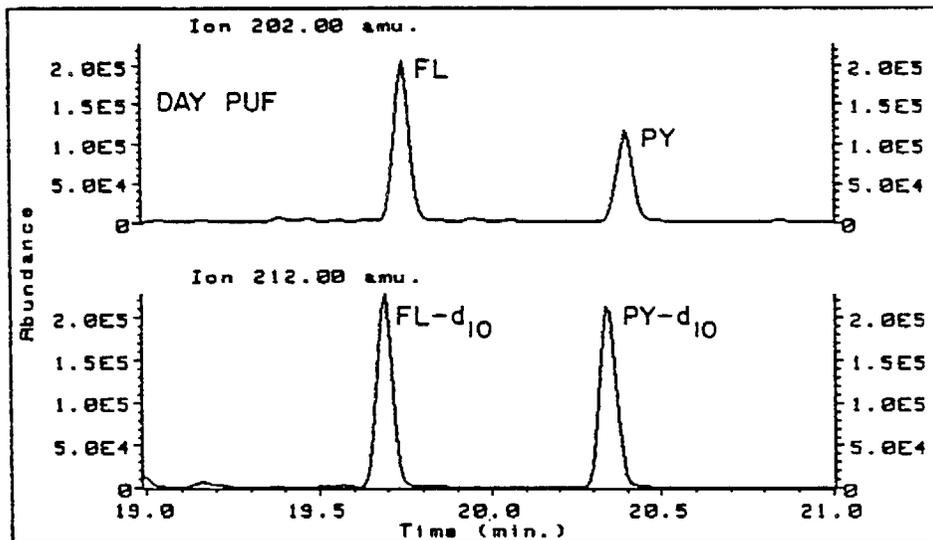


Figure VII-1. GC/MS/MID traces for the molecular ion of phenanthrene (PH) and anthracene (AN) [m/z 178] and their corresponding deuterated species (m/z 188) utilized as internal standards from the analyses of a daytime (top; Glendora Sample #1) and nighttime (bottom; Glendora Sample #2) ambient air sample collected on PUF plugs at Citrus College, Glendora, CA (from Final Report ARB Contract No. A5-150-32).

GLENDORA, CA 8/13/86 0800-2000HR



GLENDORA, CA 8/13-14/86 2000-0800HR

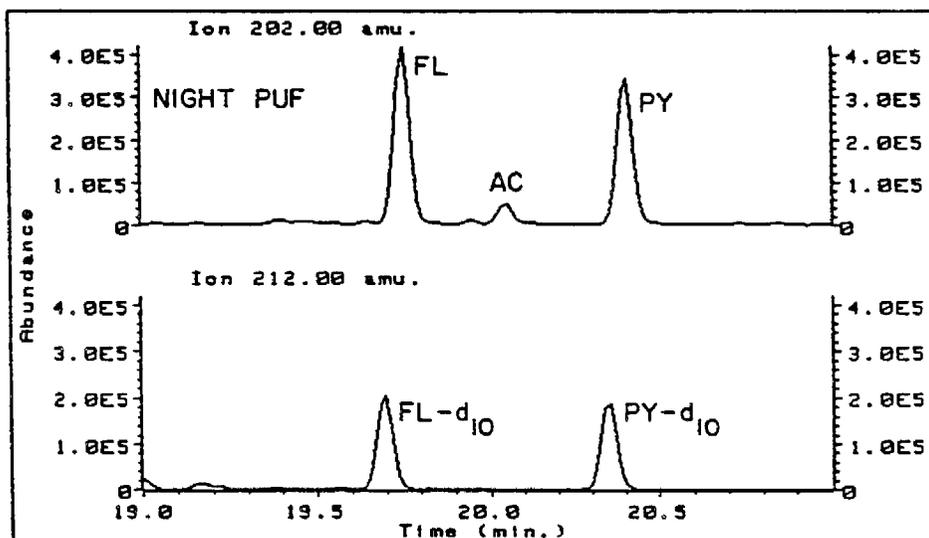


Figure VII-2. GC/MS/MID traces for the molecular ion of fluoranthene (FL), pyrene (PY) and acephenanthrylene (AC) [m/z 202] and the deuterated internal standards FL-d₁₀ and PY-d₁₀ (m/z 212) from the analyses of a daytime (top; Glendora Sample #1) and nighttime (bottom; Glendora Sample #2) ambient air sample collected on PUF plugs at Citrus College, Glendora, CA (from Final Report ARB Contract No. A5-150-32).

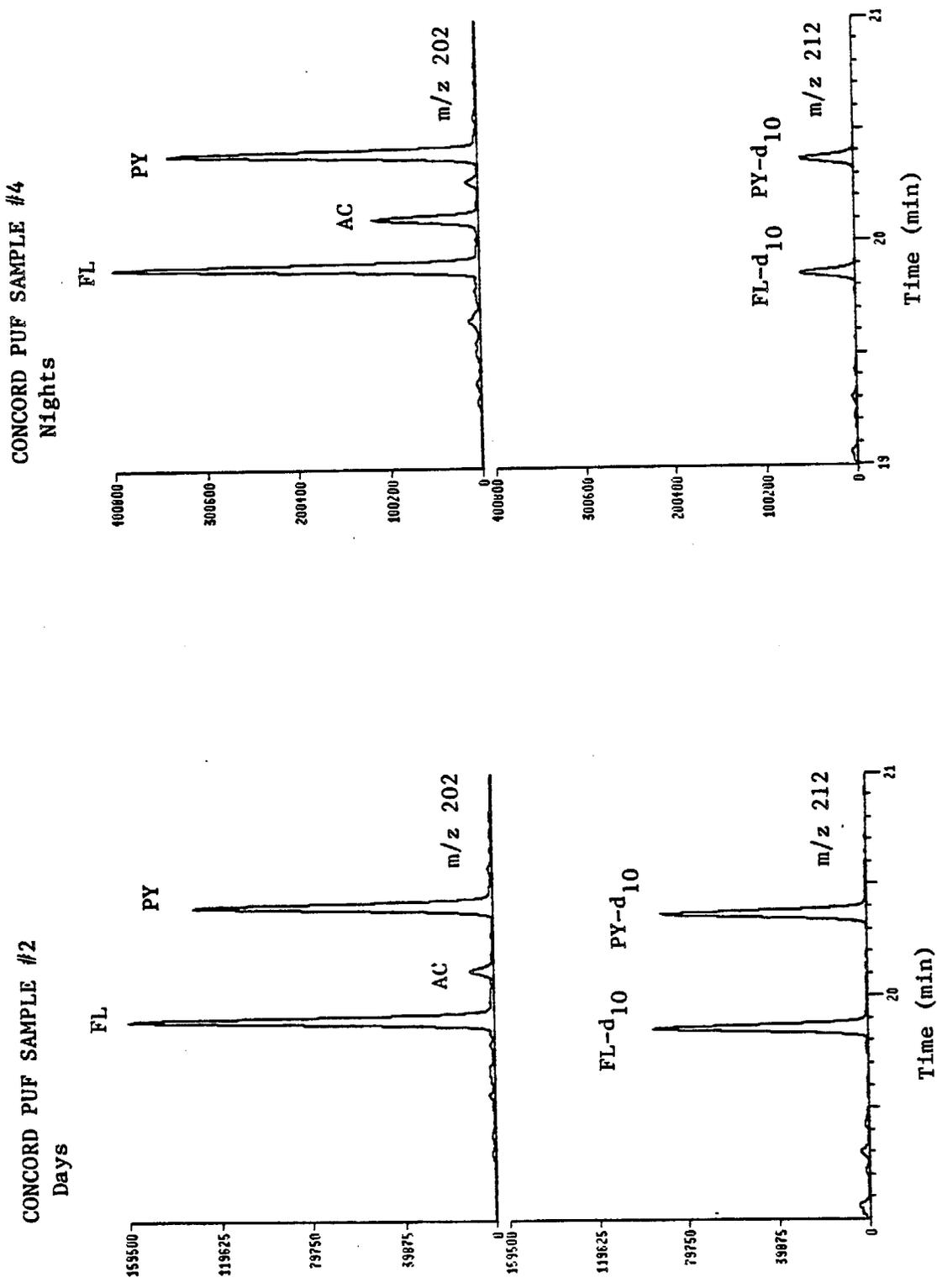


Figure VII-3. GC/MS/MID traces for the molecular ion of fluoranthene (FL), pyrene (PY) and acephenanthrylene (AC) [m/z 202] and the deuterated internal standards FL-d₁₀ and PY-d₁₀ (m/z 212) from the analyses of Concord PUF plug Sample #2, a daytime composite sample (left) and Concord PUF plug Sample #4, a nighttime composite sample (right).

Figure VII-4 shows the GC/MS/MID traces from Glendora PUF plug Sample #2 for the analysis of 1- and 2-nitronaphthalene (NN). As illustrated for the nitronaphthalenes on this figure, identifications of nitroarenes were based on the presence of several characteristic fragment ions, as well as on retention time matching of the molecular ions. Figure VII-5 shows the presence in this sample of several peaks at m/z 187 which elute after 1- and 2-nitronaphthalene. These peaks were identified as methylnitronaphthalenes (14 isomers are possible) on the basis of the presence of characteristic $[M-NO_2]^+$ and $[M-HNO_2]^+$ fragment ions as well as the m/z 187 molecular ion. In general, methylnitronaphthalenes were observed at sites where the nitronaphthalene concentrations were highest, i.e. Glendora, Reseda and Yuba City. Although we now have synthesized (under EPA funding) 12 of the 14 methylnitronaphthalene isomers (the spectra of which are given in Appendix B), isomer-specific identifications and quantifications have not yet been made.

GC/MS/MID traces of a standard mixture of the three nitrobiphenyl isomers and two isomers of nitroacenaphthene are shown in Figure VII-6. 5-Nitroacenaphthene has previously been reported in ambient air (Tokiwa et al. 1981). At Torrance, CA, during a wintertime high- NO_x episode, we did not observe nitroacenaphthene, but measured high concentrations of the isomeric species, 3-nitrobiphenyl (Arey et al. 1987). In Figure VII-7 the $[M]^+$ ions of the standard mixture are shown together with the $[M]^+$ ions and characteristic fragment ion traces obtained from the analysis of Glendora PUF plug Sample #1. As at Torrance, CA, the nitroarene isomer of M.W. 199 observed at Glendora was clearly 3-nitrobiphenyl. No nitroarene of M.W. 199 other than 3-nitrobiphenyl could be identified in the PUF plugs samples from any of the seven sites. However, at sites such as Mammoth Lakes and Concord, where high levels of PAH emissions caused interferences in the nitroarene analyses, the presence of additional isomers cannot be ruled out.

Table VII-10 gives the ambient concentrations of 1-nitronaphthalene, 2-nitronaphthalene and 3-nitrobiphenyl in the twenty-four PUF plug composite samples. The μg quantities measured for replicate GC/MS/MID analyses and the total volumes sampled are given in Table C-12. Table C-13 (from Final Report to ARB Contract No. A5-150-32) shows the separate analyses of the fourth PUF plugs from Glendora Samples #3 and #4. From

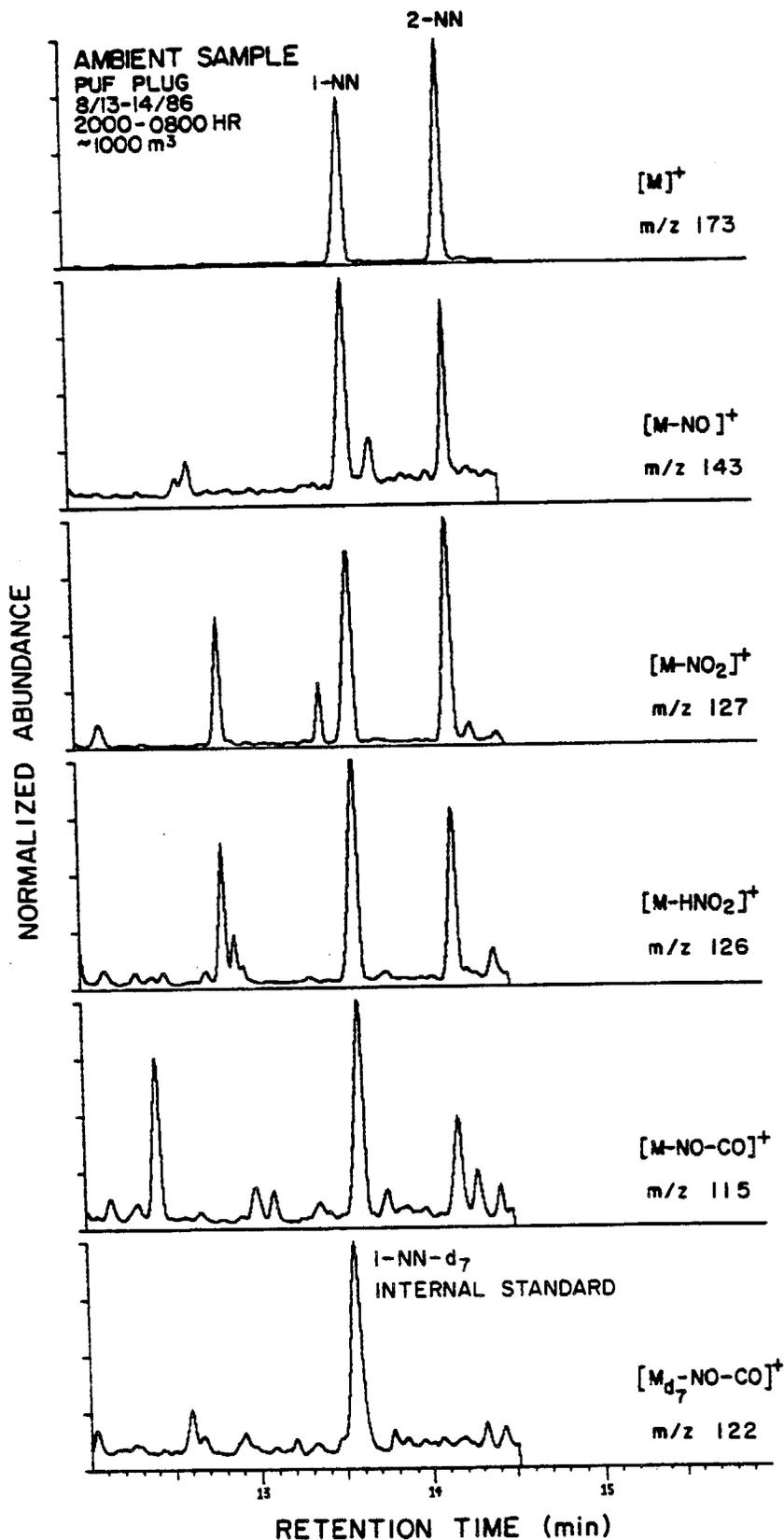


Figure VII-4. GC/MS/MID traces for the molecular ion (m/z 173) and several characteristic fragment ions of 1- and 2-nitronaphthalene (NN) and an abundant fragment ion from the deuterated internal standard 1-NN-d₇ showing the presence of 1-NN and 2-NN in an ambient air sample collected on PUF plugs at Citrus College (Glendora Sample #2) [from Final Report ARB Contract No. A5-150-32].

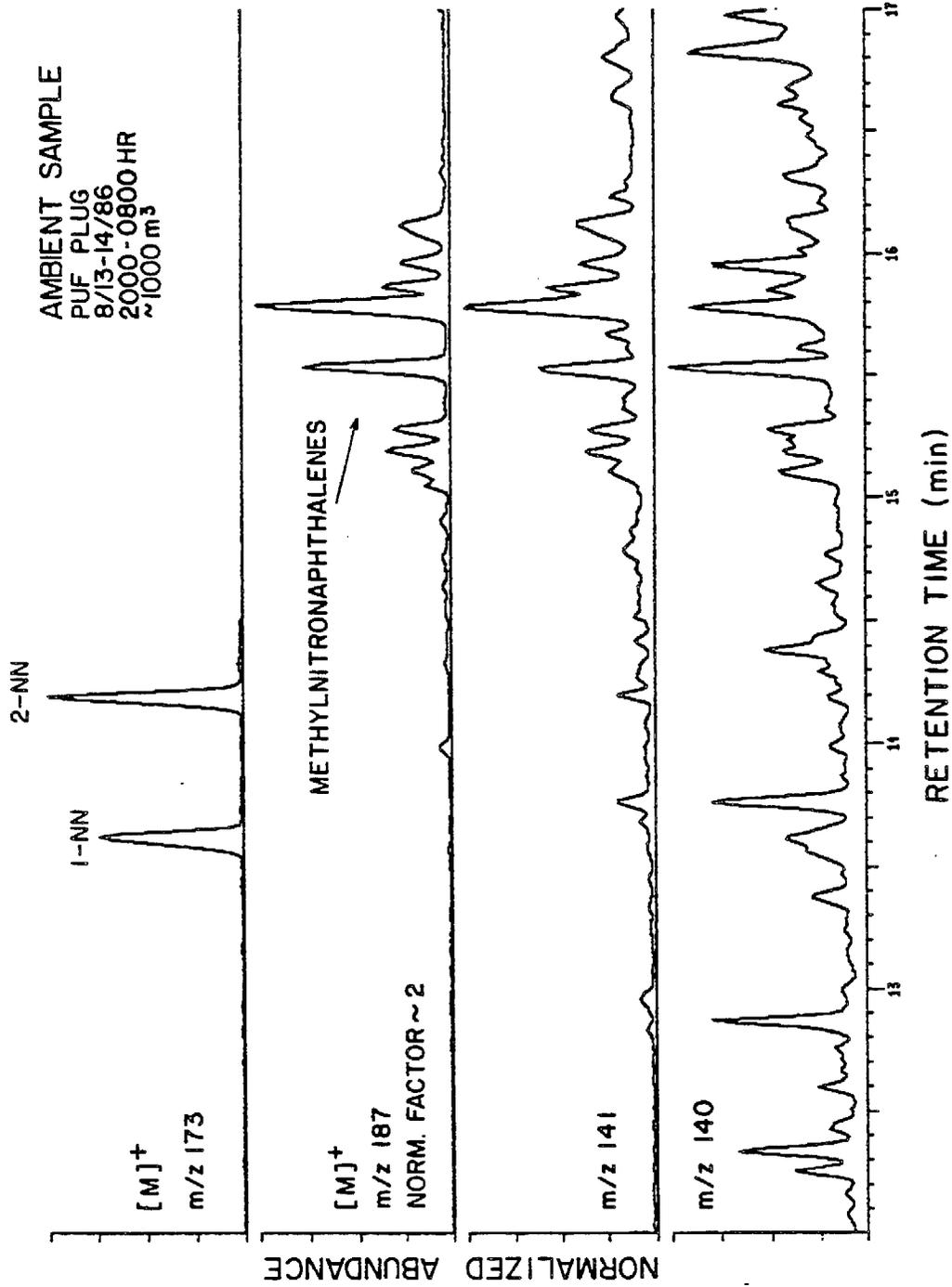


Figure VII-5. GC/MS/MID traces showing the presence of methylnitronaphthalenes in an ambient air sample collected on PUF plugs at Citrus College (Glendora Sample #2) [from Final Report ARB Contract No. A5-150-32].

NITRO-PAH STANDARD MIXTURE

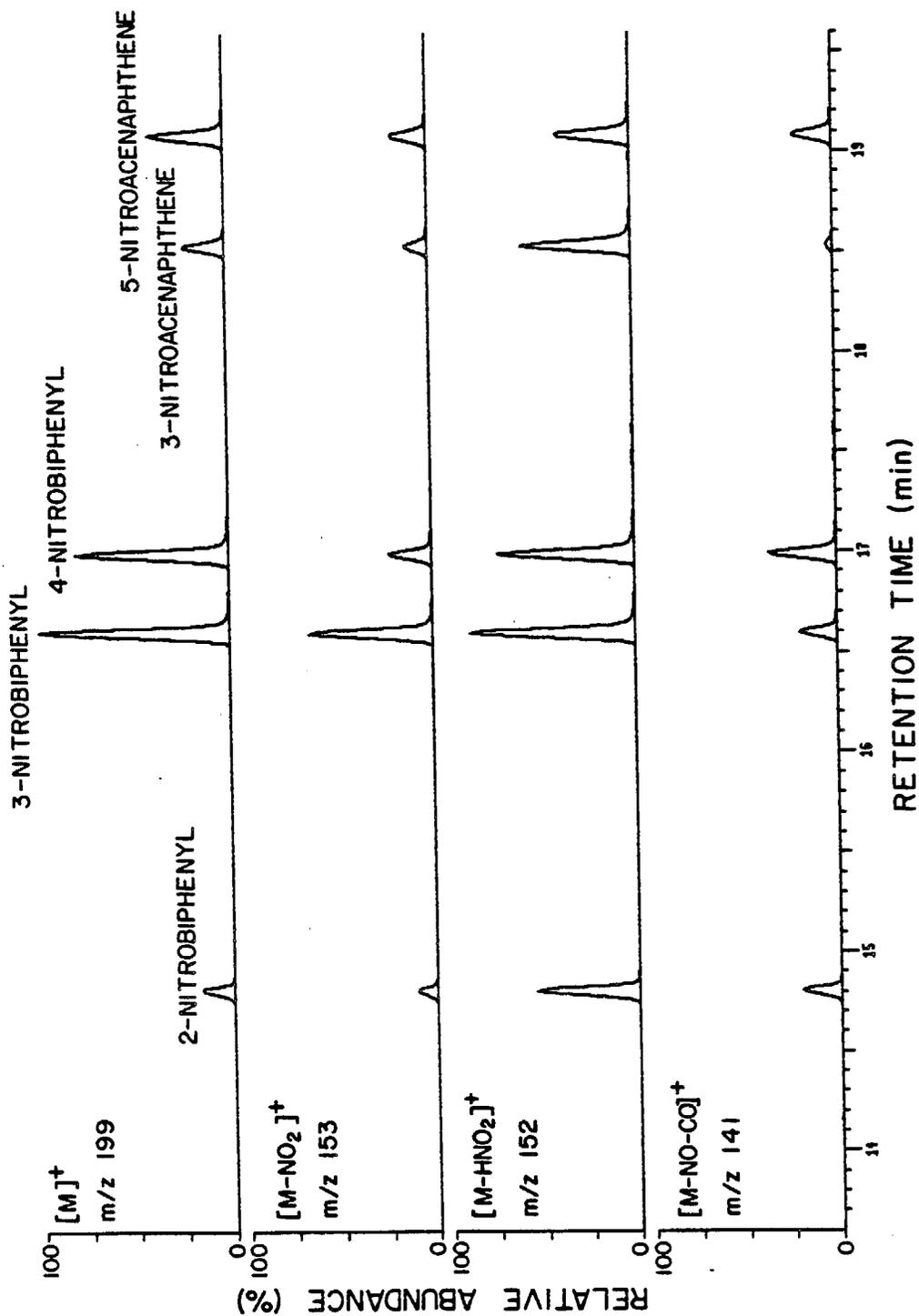


Figure VII-6. GC/MS/MID traces from the analysis of a standard mixture of the isomeric nitroacenaaphthenes and nitroacenaaphthenes showing their excellent resolution on the 30-m DB-5 capillary column utilized (from Final Report ARB Contract No. A5-150-32).

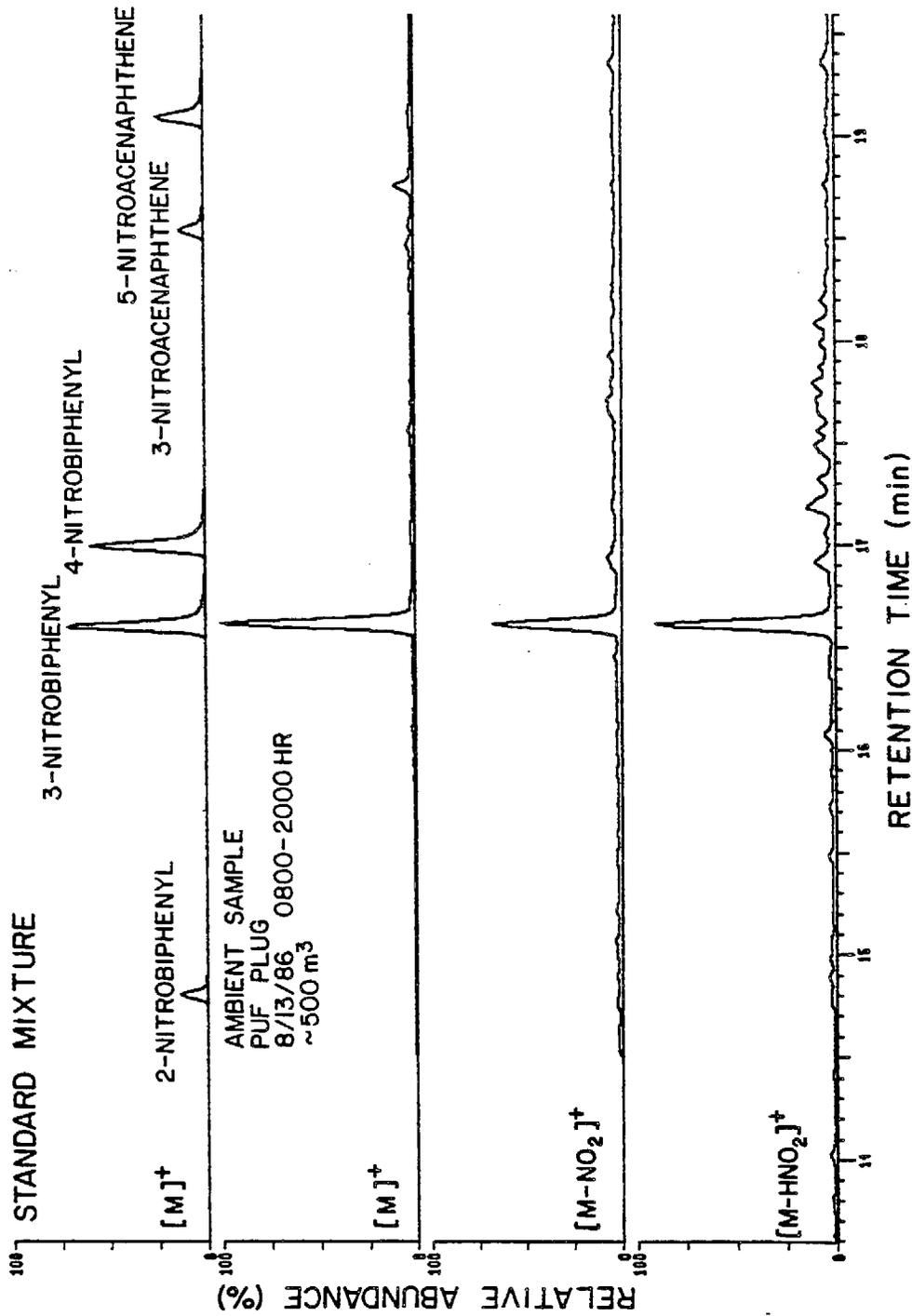


Figure VII-7. GC/MS/MID traces showing 3-nitrobiphenyl to be present in an ambient air sample collected on PUF plugs at Citrus College (Glendora Sample #1). The top trace repeats the molecular ion trace of the standard mixture (Figure VII-6) and it can be seen that the peak in the ambient sample (the molecular ion and two characteristic fragment ions shown) exactly matches 3-nitrobiphenyl in retention time (from Final Report ARB Contract No. A5-150-32).

Table VII-10. Nitroarene Concentrations Measured for Single or Composited Day/Night Sampling Intervals on PUF Plugs (pg m^{-3}) at the Seven Sites in California

Location Site and Dates ^a	pg m^{-3} b,c		
	1-Nitronaphthalene	2-Nitronaphthalene	3-Nitrobiphenyl
Glendora 8/13/86	Sample #1 Day 2,300	1,800	1,200
Glendora 8/13-14/86	Sample #2 Night 2,600	1,600	450
Glendora 8/15, 16, 17, 18/86	Sample #3 Day 2,400	2,400	850
Glendora 8/15-16, 16-17, 17-18, 18-19/86	Sample #4 Night 3,300	2,000	330
Glendora 8/20/86	Sample #5 Day 2,700	2,600	880
Glendora 8/20-21/86	Sample #6 Night 5,700	3,100	460
Yuba City 10/16, 18, 20/86	Sample #1 Day 480	610	190
Yuba City 10/17, 23/86	Sample #2 Day 470	600	130
Yuba City 10/16-17, 18-19, 20-21, 23-24/86	Sample #3 Night 460	370	69
Concord 12/8, 9/86; 1/19/87	Sample #1 Day 100	170	52

(continued)

Table VII-10 (continued) - 2

Location Site and Dates ^a	pg m ⁻³ b,c		
	1-Nitronaphthalene	2-Nitronaphthalene	3-Nitrobiphenyl
Concord 1/18,21,22/87	Day 170	Day ≤350 ^d	Day 66
Concord 12/6-7,7-8,8-9/86	Night 540	Night 260	Night 75
Concord 1/17-18,18-19,21-22/87	Night 730	Night 450	Night 120
Concord 12/10-11/86; 1/14-15/87	Night 190	Night 160	Night 28
Mammoth Lakes 2/14,16,17,21,22,26,28/87	Day ≤38 ^d	Day ≤56 ^d	Day ≤22 ^d
Mammoth Lakes 2/16-17,17-18,20-21,27-28;2/28-3/1/87	Night 180	Night 140	Night ≤59 ^d
Mammoth Lakes 2/14-15,15-16,21-22,22-23,25-26/87	Night 74	Night 64	Night ≤11 ^d
Oiledale 3/30,31/87; 4/1,2,7,8,9,10/87	Day 72	Day 120	Day 21
Oiledale 3/29-30/87; 4/9-10,10-11/87	Night 92	Night ≤140 ^d	Night 13
Oiledale 3/31-4/1/87; 4/1-2,7-8,8-9/87	Night 120	Night <180 ^e	Night 19
Reseda 5/28,29,30,31/87; 6/1,2,14,15/87	Day 340	Day 410	Day 160

(continued)

Table VII-10 (continued) - 3

Location Site and Dates ^a		pg m ⁻³ b,c		
		1-Nitronaphthalene	2-Nitronaphthalene	3-Nitrophenyl
Reseda	Sample #2 Night	810	550	49
	5/27-28, 28-29, 29-30, 30-31, 5/31-6/1; 6/1-2, 2-3, 13-14, 14-15/87			
Pt. Arguello	Sample #1 Day	15	<22 ^e	2
	7/4, 5, 6, 7, 8, 9, 10, 11, 12/87			
Pt. Arguello	Sample #2 Night	22	<61 ^e	2
	7/4-5, 5-6, 6-7, 7-8, 8-9, 9-10, 10-11, 11-12/87			

^aSee Section V for full details of compositing.

^bAverage of replicate injections.

^cFour PUF plugs in series at Glendora, three PUF plugs were used at all other sites.

^dInterference possible.

^eInterference present.

this table it can be seen that 3-nitrobiphenyl was collected quantitatively on three PUF plugs, but that some breakthrough of the nitronaphthalenes occurred. The greatest breakthrough was for 1-nitronaphthalene during the daytime collections, when the amount present on the fourth PUF plugs was ~20% of the total amount present on the first three PUFs.

Traces of 9-nitroanthracene (too low to quantify) were present on most of the PUF plug samples from Glendora. 9-Nitroanthracene was also observed on the PUF plugs samples from Reseda at estimated ambient concentration levels of 35 pg m^{-3} and 78 pg m^{-3} for Samples #1 and #2, respectively. It should be noted that 9-nitroanthracene was also observed in the filter samples (see Section VII-C below).

The generally higher levels of 3-nitrobiphenyl during the daytime collection periods at a given site suggest a daytime atmospheric formation pathway for this species. Our current knowledge of the atmospheric formation pathways of the volatile nitroarenes, as well as particle-associated species, is discussed in Section IX.

C. Filter Samples

PAH Sampled on TIGF Filters. GC/MS analysis in the full scanning mode was performed on the PAH-containing HPLC fractions (see Section VI-C) of the filter extracts of the following samples, one from each of the seven sites: Glendora Sample #3A, Yuba City Sample #2, Concord Sample #4, Mammoth Lakes Sample #2, Oildale Sample #3, Reseda Sample #1 and Pt. Arguello Sample #2. All of the total ion chromatograms (TIC) looked qualitatively similar, with the unsubstituted PAH listed in Table II-5 of M.W. range 202-276 generally being the most abundant species. The only alkyl-PAH of similar abundance to the parent PAH in certain samples (Concord #4 and Mammoth Lakes #2) was retene (1-methyl-7-isopropylphenanthrene), a marker compound for coniferous wood combustion (Ramdahl 1983). Figures VII-8 and VII-9 show the TIC from the analysis of Concord Sample #4 and Mammoth Lakes Sample #2, respectively, with the major peaks identified. Figure VII-10 shows the spectra of a standard of retene and of the compound identified as retene in Mammoth Lakes filter Sample #2.

Table VII-11 gives the concentrations of the targeted species of M.W. 202-228 listed in Table II-5 and, in addition, acephenanthrylene (M.W. 202) and retene. The μg quantities measured for replicate GC/MS/MID

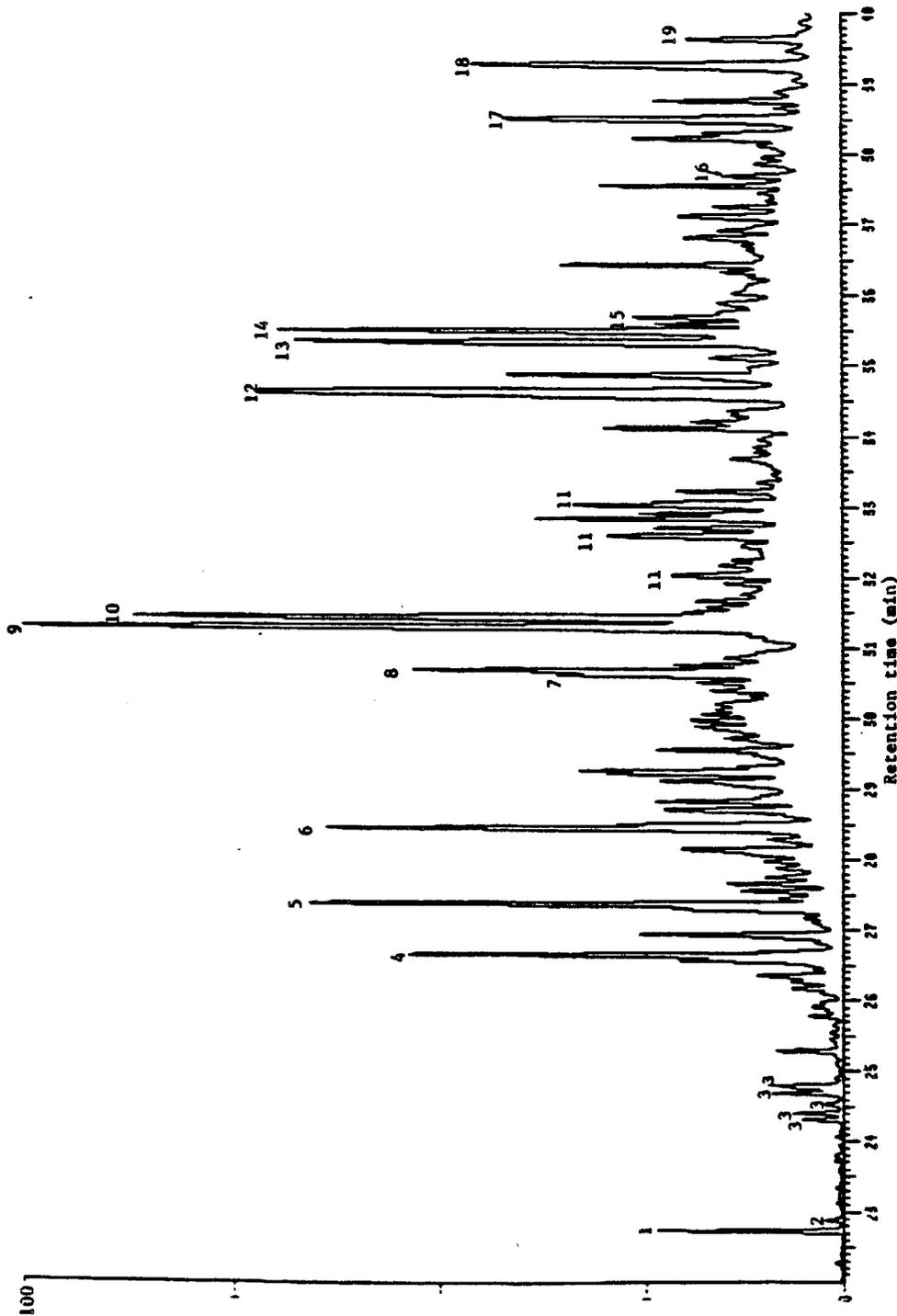


Figure VII-8. TIC of Concord filter Sample #4. Identities of the numbered peaks are as follows: (1) phenanthrene, (2) anthracene, (3) methylphenanthrenes/methylanthracenes, (4) fluoroanthrene, (5) pyrene, (6) retene, (7) benzo[c]phenanthrene, (8) benzo[ghi]fluoroanthrene, (9) benz[a]anthracene/cyclopenta[cd]pyrene, (10) chrysene/triphenylene, (11) methylbenz[a]anthracenes/methylchrysenes/methyltriphenylenes, (12) benzo[fluoro]anthrenes, (13) benzo[e]pyrene, (14) benzo[a]pyrene, (15) perylene, (16) indeno[1,2,3-cd]fluoroanthrene, (17) indeno[1,2,3-cd]pyrene, (18) benzo[ghi]perylene, (19) anthracene.

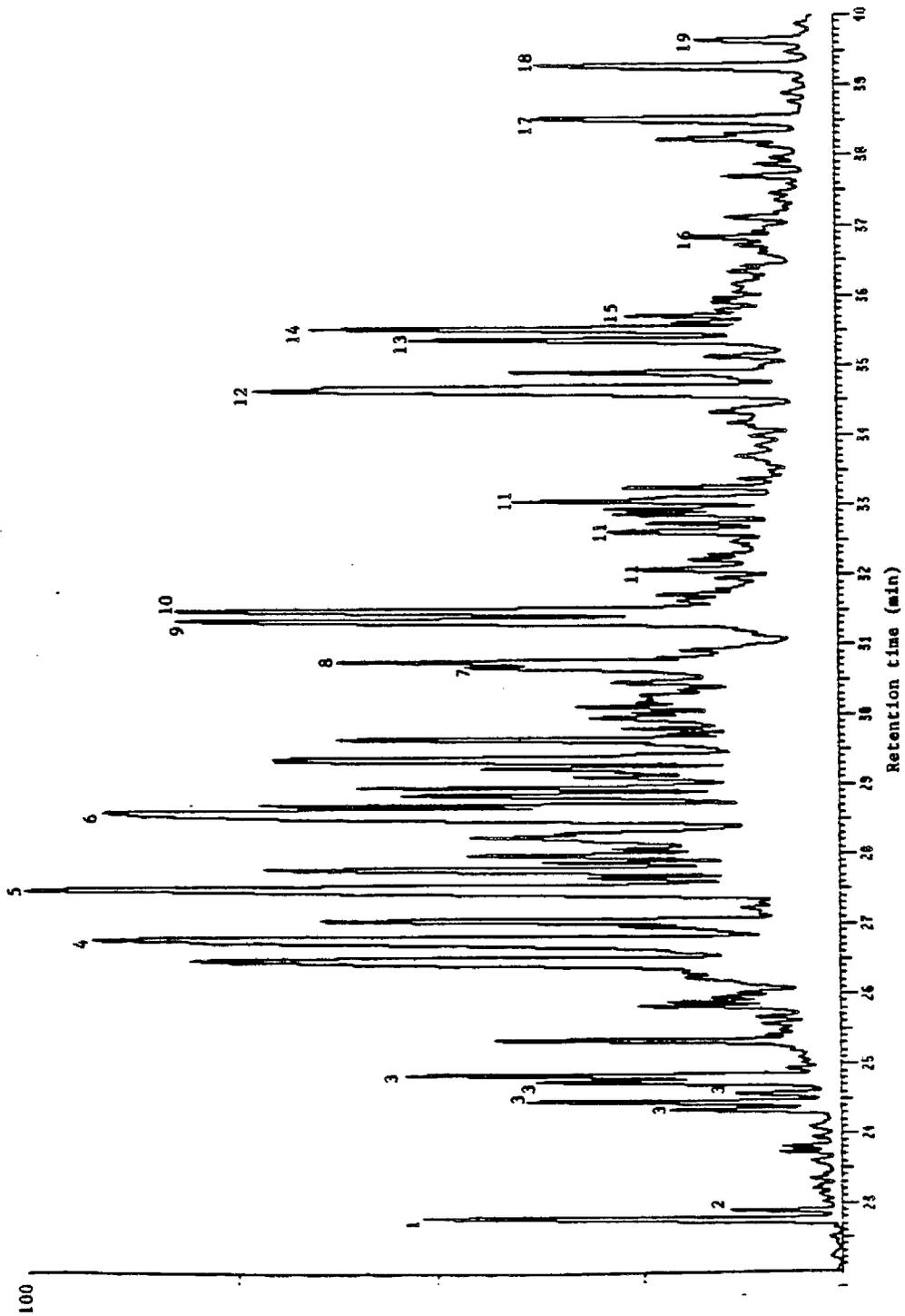
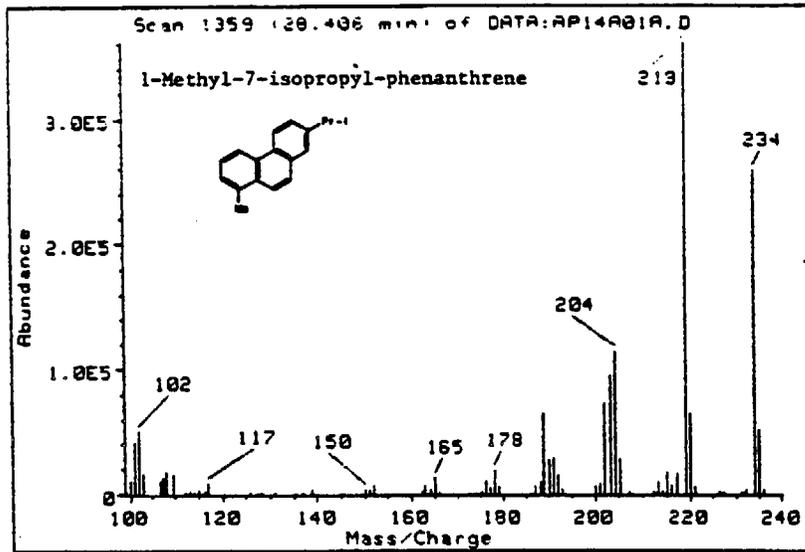
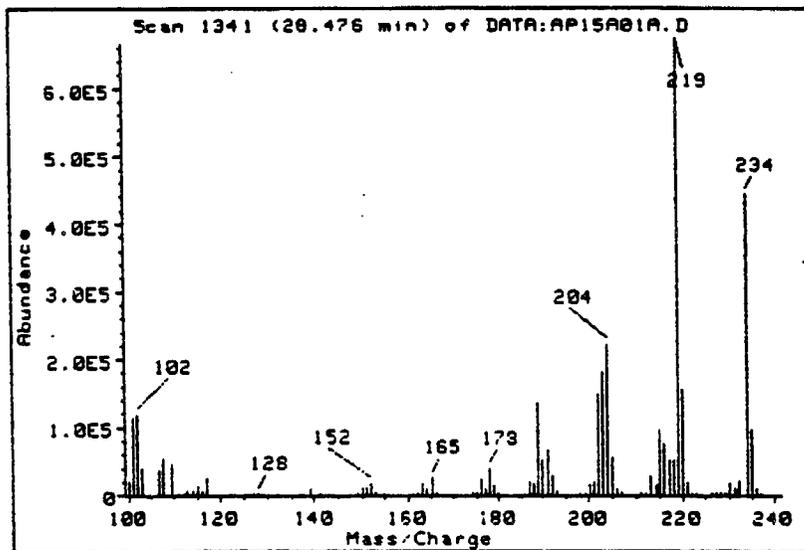


Figure VII-9. TIC of Mammoth Lakes filter Sample #2. Identities of the numbered peaks are as given on Figure VII-8.



Spectrum of retene standard.



Spectrum of compound identified as retene in Mammoth Lakes filter Sample #2.

Figure VII-10. Spectra of a retene standard (top) and the compound identified as retene in Mammoth Lakes filter Sample #2 (bottom). To quantify retene in the filter samples the molecular ion (m/z 234) and the major fragment ion (m/z 219) were monitored by GC/MS/MID.

Table VII-11. PAH Concentrations of Targeted Species H.W. 202-234 Measured for Single or Composited Day/Night Sampling Intervals on TIGF Filters (ng m⁻³) at the Seven Sampling Sites in California and San Nicolas Island

Location Site and Dates ^a	ng m ⁻³ b									
	Fluoranthene ^c	Pyrene ^c	Acphenanthrylene ^c	Benzo[ghi]-fluoranthene	Cylopenta[cd]pyrene	Benzo[ef]-phenanthrene	Benz[a]-anthracene	Chrysene/triphenylene	Retene	
Glendora 8/13/86	Sample #1 Day	0.30	0.54	0.21	0.24	0.07	0.04	0.23	0.77	0.27
Glendora 8/13-14/86	Sample #2 Night	0.28	0.33	0.03 ^d	0.38	0.18	0.03	0.28	1.47	0.14 ^d
Glendora 8/15, 16, 17, 18/86	Sample #3 Day	0.24	0.23	0.06	0.06	0.03	0.02	0.15	0.53	0.12
Glendora 8/15, 16, 17, 18/86	Sample #3A Day	0.30	0.36	0.01	0.23	0.03 ^d	0.04	0.16	1.0	0.05
Glendora 8/15-16, 16-17, 17-18, 18-19/86	Sample #4 Night	e	e	e	0.01	0.02	e	0.07	0.50	e
Glendora 8/15-16, 16-17, 17-18, 18-19/86	Sample #4A Night	0.24	0.28	0.03 ^d	0.40	0.13	0.04	0.22	1.22	0.06 ^d
Glendora 8/20/86	Sample #5 Day	0.25 ^d	0.30 ^d	e	0.16	0.08 ^d	0.03 ^d	0.15 ^d	0.83	0.02 ^d
Glendora 8/20-21/86	Sample #6 Night	0.20	0.26	0.03	0.18	0.07	0.03	0.19	0.88	0.19 ^d
Yuba City 10/16, 18, 20/86	Sample #1 Day	0.17	0.17	0.01 ^d	0.12	0.01	0.03	0.13	0.44	0.14
Yuba City 10/17, 23/86	Sample #2 Day	0.28	0.28	0.02	0.27	0.05	0.10	0.28	1.1	0.08

(continued)

Table VII-11 (continued) - 2

Location Site and Dates ^a	ng m ⁻³ b									
	Fluor- anthene ^c	Pyrene ^c	Accephenan- thrylene ^c	Benzo[ghi]- fluoranthene	Cyclopenta- [cd]pyrene	Benzo[oj]- phenanthrene	Benz[a]- anthracene	Chrysene/ triphenylene	Retene	
Yuba City Sample #3 Night 10/16-17, 18-19, 20-21, 23-24/86	0.17	0.19	0.03	0.15	0.11	0.03	0.16	0.49	0.12	
Concord Sample #1 Day 12/8, 9/86; 1/19/87	0.19	0.23	0.03	0.73	0.84	1.9	1.6	2.5	0.15	
Concord Sample #2 Day 1/18, 21, 22/87	0.21	0.23	0.03	0.85	0.47	0.33	2.5	4.6	0.23	
Concord Sample #3 Night 12/6-7, 7-8, 9/86	0.53	0.64	0.20	2.2	6.0	1.3	6.3	8.9	1.4	
Concord Sample #4 Night 1/17-18, 18-19, 21-22/87	1.2	1.4	0.44	3.6	9.3	2.0	9.7	13.5	2.2	
Concord Sample #5 Night 12/10-11/86; 1/14-15/87	0.17	0.20	0.04	0.81	1.6	0.33	2.1	3.0	0.21	
Mammoth Lakes Sample #1 Day 2/14, 16, 17, 21, 22, 26, 28/87	4.8	5.5	1.4	2.6	3.3	1.6	5.2	6.5	7.1	
Mammoth Lakes Sample #2 Night 2/16-17, 17-18, 20-21, 27-28; 2/28-3/1/87	29.6	29.8	8.9	8.8	11.8	7.0	18.3	23.6	85.7	
Mammoth Lakes Sample #3 Night 2/14-15, 15-16, 21-22, 22-23, 25-26/87	7.3	7.5	2.4	2.1	3.3	1.6	5.0	6.2	28.6	
Oildale Sample #1 Day 3/30, 31/87; 4/1, 2, 7, 8, 9, 10/87	0.27	0.30	0.02	0.10	0.05	0.06	0.32	0.54	0.03	
Oildale Sample #2 Night 3/29-30/87; 4/9-10, 10-11/87	0.17	0.18	0.02	0.09	0.03	0.03	0.13	0.30	0.14	

(continued)

Table VII-11 (continued) - 3

Location Site and Dates ^a		ng m ⁻³ b									
		Fluor- anthene ^c	Pyrene ^c	Acophenan- thrylene ^c	Benzofl[ghi]- fluoranthene	Cyclopenta- [cd]pyrene	Benzo[ghi]- phenanthrene	Benz[ghi]- anthracene	Chrysenes/ triphenylene	Retene	
Oilidale	Sample #3 Night 3/31-4/1/87; 4/1-2,7-8,8-9/87	0.52	0.62	0.03	0.19	0.08	0.10	0.68	1.05	0.10	
Reseda	Sample #1 Day 5/28,29,30,31/87; 6/1,2,14,15/87	0.28	0.33	0.08	0.31	0.29	0.07	0.32	0.67	0.05	
Reseda	Sample #2 Night 5/27-28,28-29,29-30,30-31,5/31-6/1; 6/1-2,2-3,13-14,14-15/87	0.15	0.16	0.02	0.11	0.05	0.02	0.13	0.32	0.03	
Pt. Arguello	Sample #1 Day 7/4,5,6,7,8,9,10,11,12/87	0.11	0.06	e	0.01	e	0.005	0.004	0.05	0.03	
Pt. Arguello	Sample #2 Night 7/4-5,5-6,6-7,7-8,8-9,9-10,10-11, 11-12/87	0.16	0.10	e	0.01	e	0.005	0.01	0.05	0.04	
San Nicolas Island	Composite 6/19,24,25/87; 7/13,14,15/87; 8/27,28,29/87; 9/2,3/87; 6/19-20, 24-25,25-26/87; 7/13-14,14-15, 15-16/87; 8/27-28,28-29,29-30/87; 9/3-4/87	0.04	0.07	e	0.01	e	0.004	0.01	0.05	0.06	

^aSee Section V for full details of compositing.^bAverage of replicate injections.^cMainly present on PUF plugs, see text for discussion.^dValue for a single GC/MS injection.^eNone detected or present in trace amounts too low to quantify.

analyses and the total volumes for the composite samples are given in Table C-14. Comparison of the concentrations of fluoranthene and pyrene measured from the PUF plug samples (Table VII-9) with those given in Table VII-11 from the filter samples shows that, in general, most of the ambient fluoranthene and pyrene was not present on the filters. Thus, the fluoranthene and pyrene was either present in the gas phase or was blown-off the filters during sampling.

Table VII-12 gives the percentages of the total (the sum of the concentrations collected on the PUF plugs and the TIGF filters) ambient fluoranthene and pyrene present on the TIGF filters at each site. Only a small fraction (<30%) of the fluoranthene and pyrene were present on the filters samples, except for those collected at Mammoth Lakes and at Pt. Arguello. The high fractions observed on the filter samples at Mammoth Lakes is consistent with the low ambient temperatures (see Table X-2) at which sampling occurred. At Pt. Arguello, the ambient temperatures were similar to those encountered at sites where most of the fluoranthene and pyrene was found on the PUF plugs. A plausible explanation for these findings is that the low levels of PAH present at Pt. Arguello represent PAH transported over a long distance and the PAH which remain may be tightly particle-bound or trapped within the particles.

Although the more volatile species phenanthrene and anthracene are identified on the total ion chromatograms of the Concord and Mammoth Lakes samples shown in Figures VII-8 and VII-9, respectively, the amounts present on the filters were only a small fraction of the ambient concentrations. It is estimated that the phenanthrene and anthracene in Concord filter Sample #4 (Figure VII-8) represent <0.5% of the ambient concentrations, and even for Mammoth Lakes filter Sample #2 (Figure VII-9) which was collected at the lowest ambient temperatures, the amounts of phenanthrene and anthracene present on the filter are estimated to be ~10% of the ambient concentrations.

The electron impact mass spectra of benz[a]anthracene and chrysene given in Figure VII-11 are typical of most PAH, consisting mainly of an intense molecular ion peak and small ion peaks due to the loss of one to four hydrogen atoms. Due to the simplicity and non-specificity of these spectra, isomer-specific PAH identification depends on chromatographic resolution and retention time matching of the molecular ion peak with that

Table VII-12. Percentage of the Total Ambient Fluoranthene and Pyrene Present on TIGF Filter Samples at the Seven Sampling Sites in California

Location Site and Dates ^a			Fluoranthene ^b	Pyrene ^c
Glendora 8/13/86	Sample #1	Day	7	18
Glendora 8/13-14/86	Sample #2	Night	4	6
Glendora 8/15, 16, 17, 18/86	Sample #3	Day	5	9
Glendora 8/15-16, 16-17, 17-18, 18-19/86	Sample #4	Night	4	6
Glendora 8/20/86	Sample #5	Day	4	8
Glendora 8/20-21/86	Sample #6	Night	3	5
Yuba City 10/16, 18, 20/86	Sample #1	Day	5	8
Yuba City 10/17, 23/86	Sample #2	Day	12	20
Yuba City 10/16-17, 18-19, 20-21, 23-24/86	Sample #3	Night	9	13
Concord 12/8, 9/86; 1/19/87	Sample #1	Day	2	3
Concord 1/18, 21, 22/87	Sample #2	Day	3	4
Concord 12/6-7, 7-8, 8-9/86	Sample #3	Night	3	4
Concord 1/17-18, 18-19, 21-22/87	Sample #4	Night	5	6
Concord 12/10-11/86; 1/14-15/87	Sample #5	Night	2	3
Mammoth Lakes 2/14, 16, 17, 21, 22, 26, 28/87	Sample #1	Day	34	40

(continued)

Table VII-12 (continued) - 2

Location Site and Dates ^a	Fluoranthene ^b	Pyrene ^c
Mammoth Lakes Sample #2 Night 2/16-17, 17-18, 20-21, 27-28; 2/28-3/1/87	65	71
Mammoth Lakes Sample #3 Night 2/14-15, 15-16, 21-22, 22-23, 25-26/87	64	63
Oildale Sample #1 Day 3/30, 31/87; 4/1, 2, 7, 8, 9, 10/87	17	19
Oildale Sample #2 Night 3/29-30/87; 4/9-10, 10-11/87	13	14
Oildale Sample #3 Night 3/31-4/1/87; 4/1-2, 7-8, 8-9/87	24	28
Reseda Samples #1 Day 5/28, 29, 30, 31/87; 6/1/2, 14, 15/87	6	9
Reseda Sample #2 Night 5/27-28, 28-29, 29-30, 30-31, 5/31-6/1; 6/1-2, 2-3, 13-14, 14-15/87	4	4
Pt. Arguello Sample #1 Day 7/4, 5, 6, 7, 8, 9, 10, 11, 12/87	-50	-40
Pt. Arguello Sample #2 Night 7/4-5, 5-6, 6-7, 7-8, 8-9, 9-10, 10-11, 11-12/87	-45	-40

^aSee Section V for full details of compositing.

^bFluoranthene filter/(Fluoranthene filter + Fluoranthene PUF) x 100.

^cPyrene filter/(Pyrene filter + Pyrene PUF) x 100.

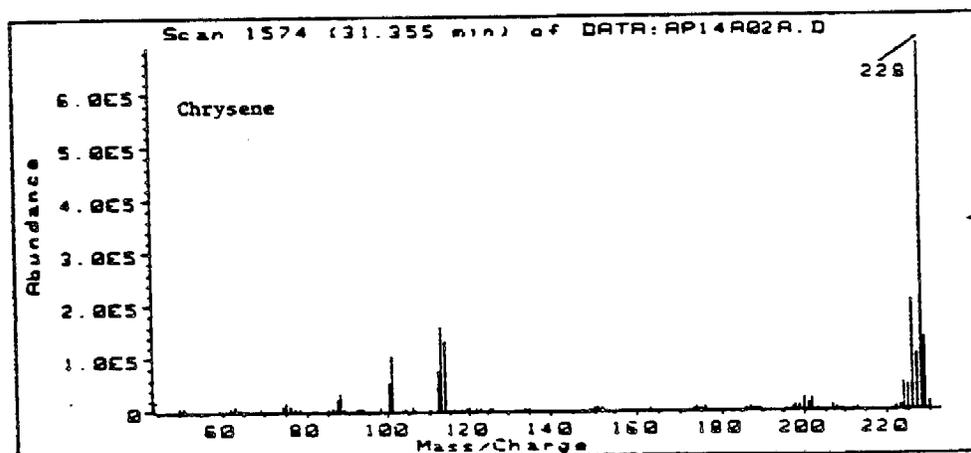
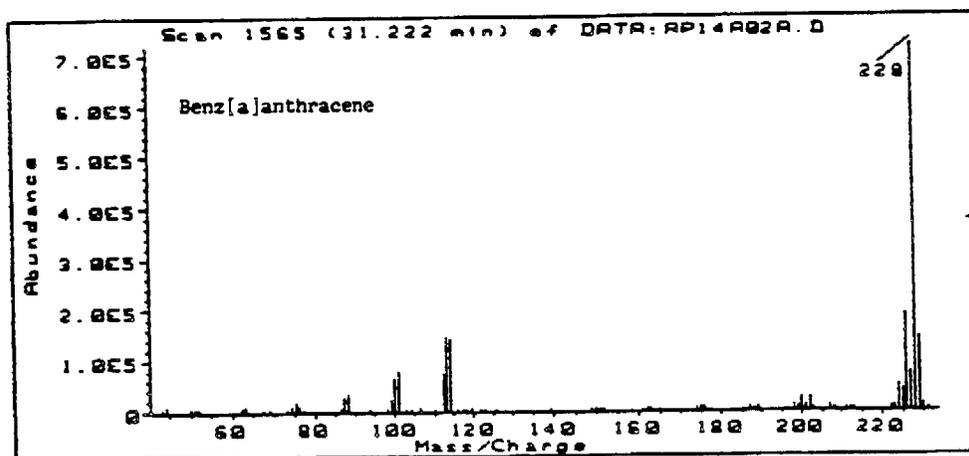


Figure VII-11. Electron impact mass spectra of benz[a]anthracene and chrysene.

of an authentic standard. GC/MS/MID analyses of standard solutions of the targeted PAH of M.W. 226 and 228 are shown in Figure VII-12. As seen from this figure, chrysene and triphenylene (M.W. 228) co-elute on the GC column used, and the ambient concentrations given in Table VII-11 are the sums of these two species. Additionally benz[a]anthracene (M.W. 228) co-elutes with cyclopenta[cd]pyrene (M.W. 226) and benzo[c]phenanthrene (M.W. 228) is not completely resolved from benzo[ghi]fluoranthene (M.W. 226), therefore, the areas of the M.W. 226 species used for quantification were corrected for the contribution of the $[M-2]^+$ ion of the co-eluting M.W. 228 species. GC/MS/MID traces from the analyses of two typical ambient POM filter samples for the M.W. 226 and 228 PAH are shown in Figure VII-13. Note the presence of the deuterated internal standards, benz[a]-anthracene- d_{12} and chrysene- d_{12} (m/z 240 ion trace), which were used both for retention time markers and for quantification.

Table VII-13 gives the ambient concentrations measured for the M.W. 252 species on the targeted list, including benzo[a]pyrene. The μg quantities measured for replicate GC/MS/MID analyses and the total sample volumes are given in Table C-15. Figure VII-14 shows MID traces from the analysis of standard solutions of the targeted M.W. 252 PAH and the deuterated internal standards employed. Benzo[e]pyrene elutes just prior to, and benzo[a]pyrene just after, benzo[a]pyrene- d_{12} . As seen from this figure, benzo[b]fluoranthene is resolved from benzo[k]fluoranthene (the two benzofluoranthene species present in SRM 1647), but benzo[j]fluoranthene elutes between these two isomers. Therefore, the sum of these benzofluoranthenes is reported in Table VII-13.

Figure VII-15 gives GC/MS/MID traces from the analyses of two of the ambient filter samples for the M.W. 252 PAH. As seen from this figure, perylene could be readily identified and quantified, and is therefore, also reported in Table VII-13. An additional small peak on the traces in Figure VII-15 has been tentatively identified as benzo[a]fluoranthene on the basis of its elution after the other benzofluoranthenes but prior to benzo[e]pyrene (Wise et al. 1986).

As discussed in Section VI-C, the PAH of M.W. >252 were distributed between the HPLC fraction collected as the PAH-fraction (7-22 min) and the HPLC fraction in which the nitroarenes elute (22-34 min; see Scheme VI-1). Since the deuterated internal standard originally added for

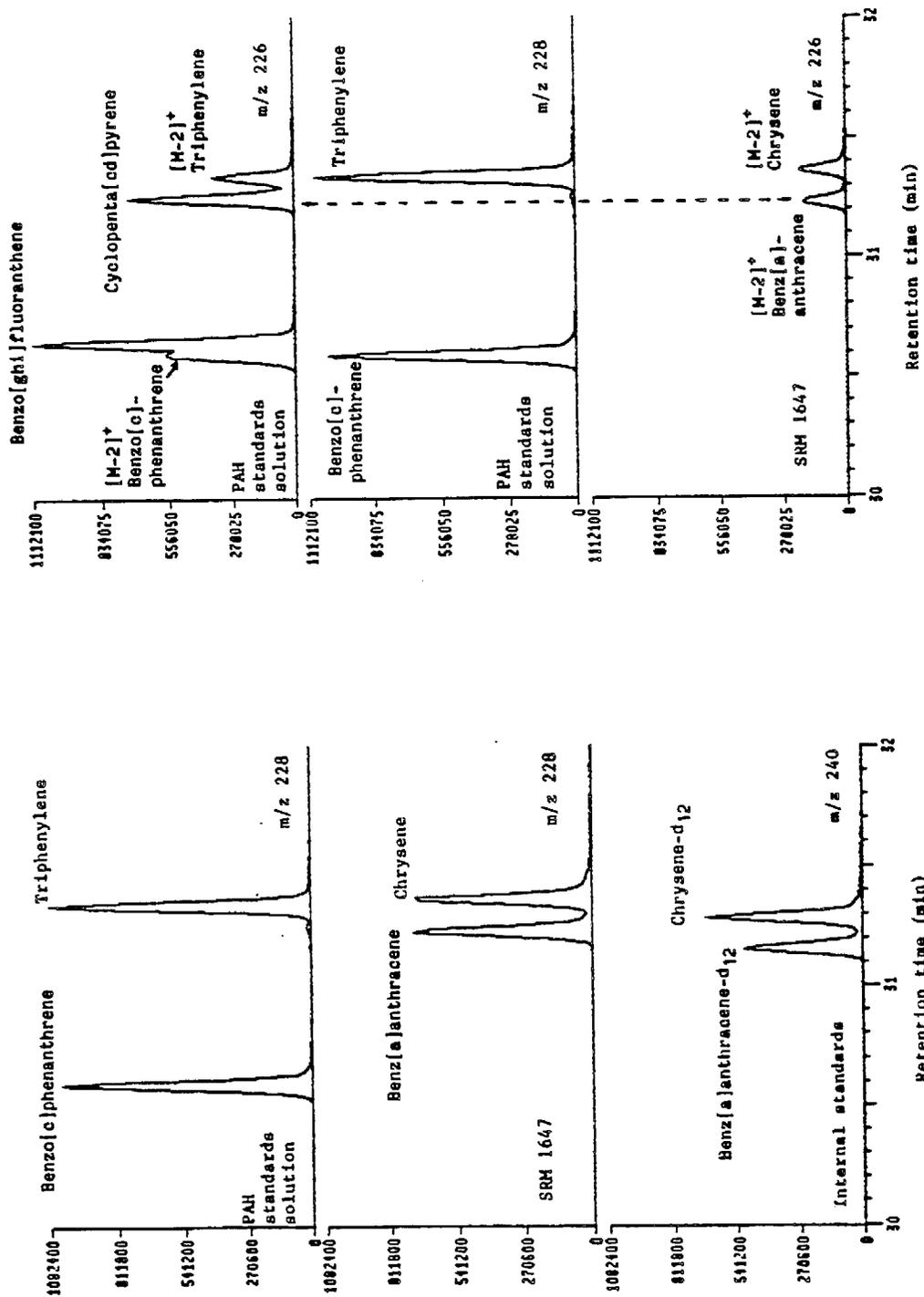


Figure VII-12. MID traces from the GC/MS/MID analyses of the SRM 1647 standard PAH solution (spiked with deuterated internal standards) and a standard solution consisting of the deuterated internal standards and those PAH to be monitored which were not present in the SRM. The left side of the figure shows the deuterated internal standards eluting just prior to their non-deuterated analogues. Since, as shown, chrysene and triphenylene cannot be resolved, their concentration in ambient POM has been reported as the sum of the two species (see Table VII-11). The right side of the figure shows that in the analyses of the M.W. 226 species, the benzo[ghi]fluoranthene peak must be corrected for the contribution of the [M-2]⁺ ion of benzo[c]phenanthrene and the cyclopenta[cd]pyrene peak must be corrected for the [M-2]⁺ peak of benz[a]anthracene.

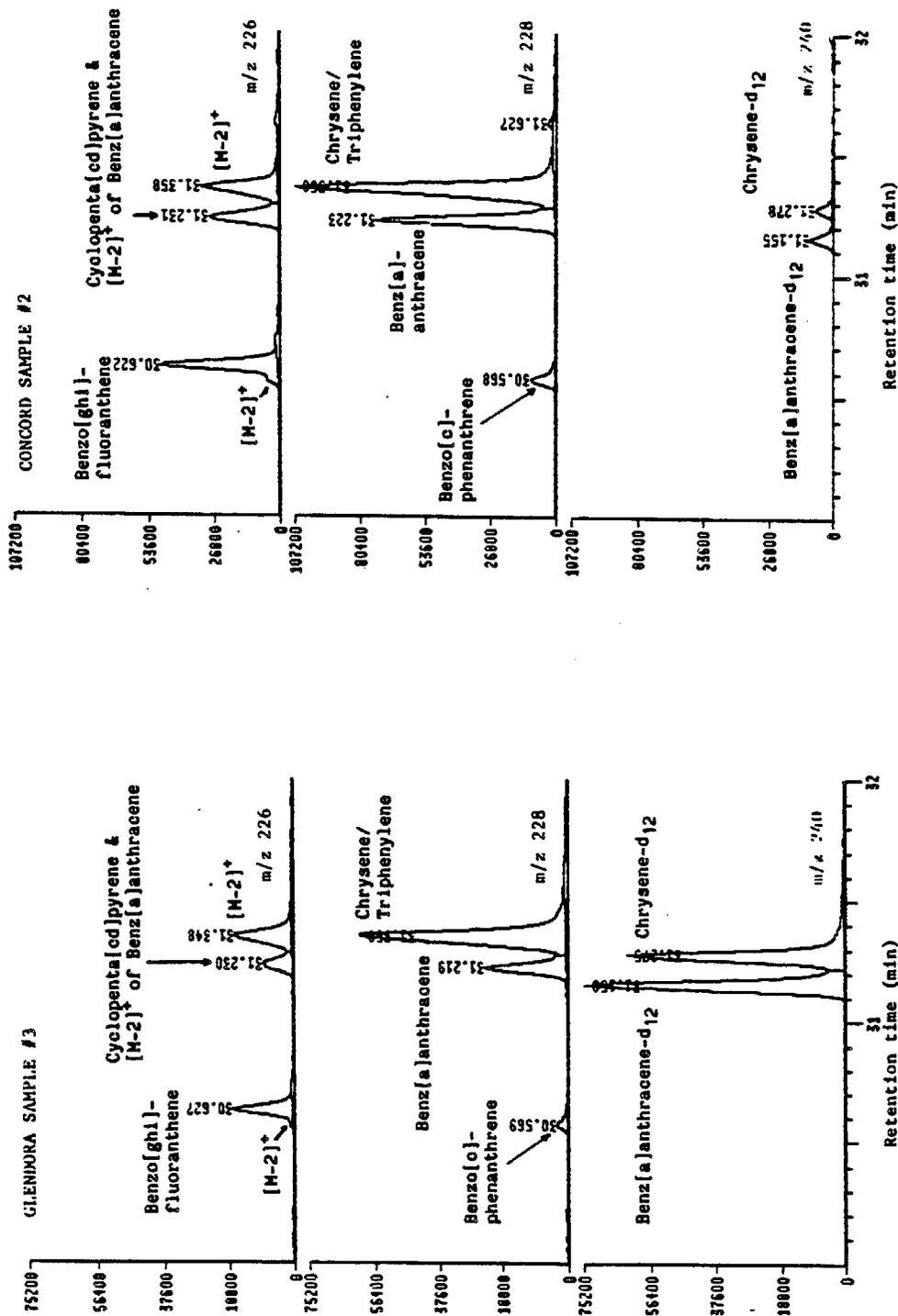


Figure VII-13. MID traces from the GC/MS/MID analysis of two ambient POM filter samples for the M.W. 228 and 226 species. Note that for Glendora Sample #3 (left) the internal standard spikes more closely matched the amounts of the M.W. 228 species present in the POM. Concord Sample #2 (right) was spiked proportionately (on the basis of the particle weights collected) showing that the PAH/particle weight ratio at Concord was significantly higher than at Glendora.

Table VII-13. The M.W. 252 Species: Benzo[fluoranthene], Benzo[e]pyrene, Benzo[a]pyrene and Perylene Measured for Single or Compositied Day/Night Sampling Intervals on TIGF Filters at the Seven Sampling Sites in California and San Nicolas Island

Location Site and Dates ^a	ng m ⁻³ b				
	Benzo- fluoranthenes ^c	Benzo[e]- pyrene	Benzo[a]- pyrene	Benzo[a]- pyrene	Perylene ^d
Glendora 8/13/86	Sample #1 Day	1.17	0.62	0.26	0.06
Glendora 8/13-14/86	Sample #2 Night	2.43	1.54	0.62	0.19
Glendora 8/15, 16, 17, 18/86	Sample #3 Day	0.80	0.41	0.18	0.04
Glendora 8/15, 16, 17, 18/86	Sample #3A Day	0.97	0.56	0.21	e
Glendora 8/15-16, 16-17, 17-18, 18-19/86	Sample #4 Night	1.32	0.65	0.18	0.07
Glendora 8/15-16, 16-17, 17-18, 18-19/86	Sample #4A Night	1.54	1.13	0.36	0.07
Glendora 8/20/86	Sample #5 Day	1.76	0.83	0.23	0.07
Glendora 8/20-21/86	Sample #6 Night	1.88	0.95	0.32	0.10
Yuba City 10/16, 18, 20/86	Sample #1 Day	0.65	0.35	0.13	0.02
Yuba City 10/17, 23/86	Sample #2 Day	1.50	0.66	0.32	0.05

(continued)

Table VII-13 (continued) - 2

Location Site and Dates ^a	ng m ⁻³ b			
	Benzo- fluoranthenes ^c	Benzo[e]- pyrene	Benzo[a]- pyrene	Perylene ^d
Yuba City Sample #3 Night 10/16-17, 18-19, 20-21, 23-24/86	0.65	0.34	0.22	0.05
Concord Sample #1 Day 12/8, 9/86; 1/19/87	4.42	1.91	1.77	0.38
Concord Sample #2 Day 1/18, 21, 22/87	5.73	2.77	3.23	0.36
Concord Sample #3 Night 12/6-7, 7-8, 8-9/86	11.06	4.22	6.15	1.39
Concord Sample #4 Night 1/17-18, 18-19, 21-22/87	15.53	5.76	8.15	1.67
Concord Sample #5 Night 12/10-11/86; 1/14-15/87	3.98	1.52	1.93	0.38
Mammoth Lakes Sample #1 Day 2/14, 16, 17, 21, 22, 26, 28/87	7.25	2.57	3.56	0.77
Mammoth Lakes Sample #2 Night 2/16-17, 17-18, 20-21, 27-28; 2/28-3/1/87	23.20	8.00	12.49	2.76
Mammoth Lakes Sample #3 Night 2/14-15, 15-16, 21-22, 22-23, 25-26/87	6.12	2.05	3.14	0.64
Oildale Sample #1 Day 3/30, 31/87; 4/1, 2, 7, 8, 9, 10/87	0.80	0.44	0.42	0.15
Oildale Sample #2 Night 3/29-30/87; 4/9-10, 10-11/87	0.43	0.25	0.17	0.04

(continued)

Table VII-13 (continued) - 3

Location Site and Dates ^a	ng m ⁻³ b			
	Benzo- fluoranthenes ^c	Benzo[e]- pyrene	Benzo[a]- pyrene	Perylene ^d
Oildale Sample #3 Night 3/31-4/1/87; 4/1-2,7-8,8-9/87	2.19	0.98	0.88	0.34
Reseda Sample #1 Day 5/28,29,30,31/87; 6/1,2,14,15/87	0.94	0.71	0.47	0.11
Reseda Sample #2 Night 5/27-28,28-29,29-30,30-31,5/31-6/1; 6/1-2,2-3,13-14,14-15/87	0.44	0.28	0.13	0.02
Pt. Arguello Sample #1 Day 7/4,5,6,7,8,9,10,11,12/87	e	0.005	e	e
Pt. Arguello Sample #2 Night 7/4-5,5-6,6-7,7-8,8-9,9-10,10-11,11-12/87	e	0.008	e	e
San Nicolas Island Composite 6/19,24,25; 7/13,14,15; 8/27,28,29; 9/2,3/87; 6/19-20,24-25,25-26/87; 7/13-14,14-15,15-16/87; 8/27-28,28-29,29-30/87; 9/3-4/87	0.01 ^f	0.005	e	e

^aSee Section V for full details of compositing.

^bAverage of replicate GC/MS injections.

^c Benzo[b]fluoranthene; benzo[j]fluoranthene and benzo[k]fluoranthene.

^dNot on targeted list of PAH.

^eAmount present too low to quantify.

^fValue from a single GC/MS injection.

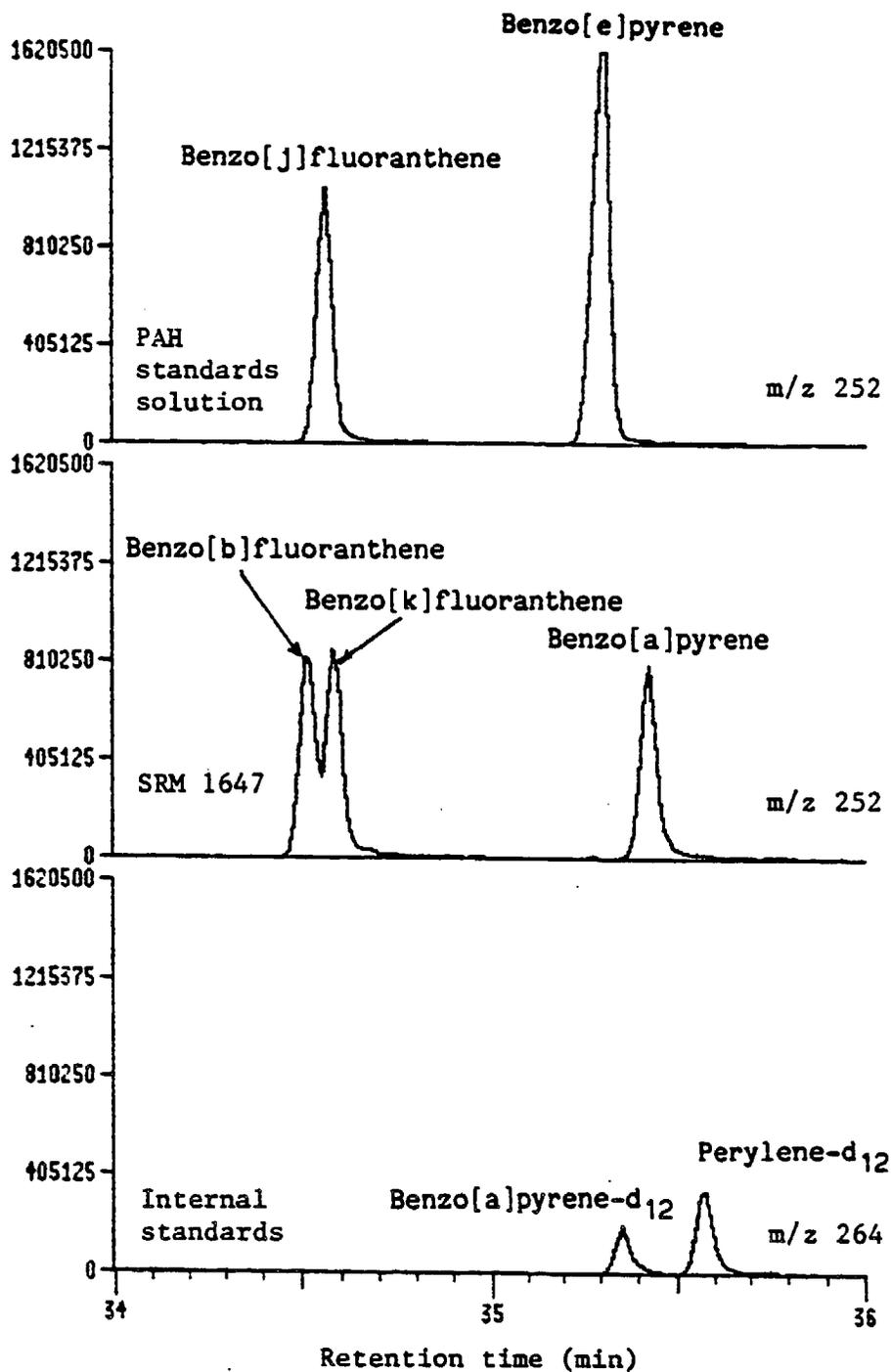


Figure VII-14. MID traces from the GC/MS/MID analyses of the SRM 1647 standard PAH solution (spiked with deuterated internal standards) and a standard solution consisting of the deuterated internal standards and those PAH to be monitored which were not present in the SRM. It can be seen that benzo[e]pyrene and benzo[a]pyrene are well resolved on the GC column used, but that the three benzofluoranthenes will overlap.

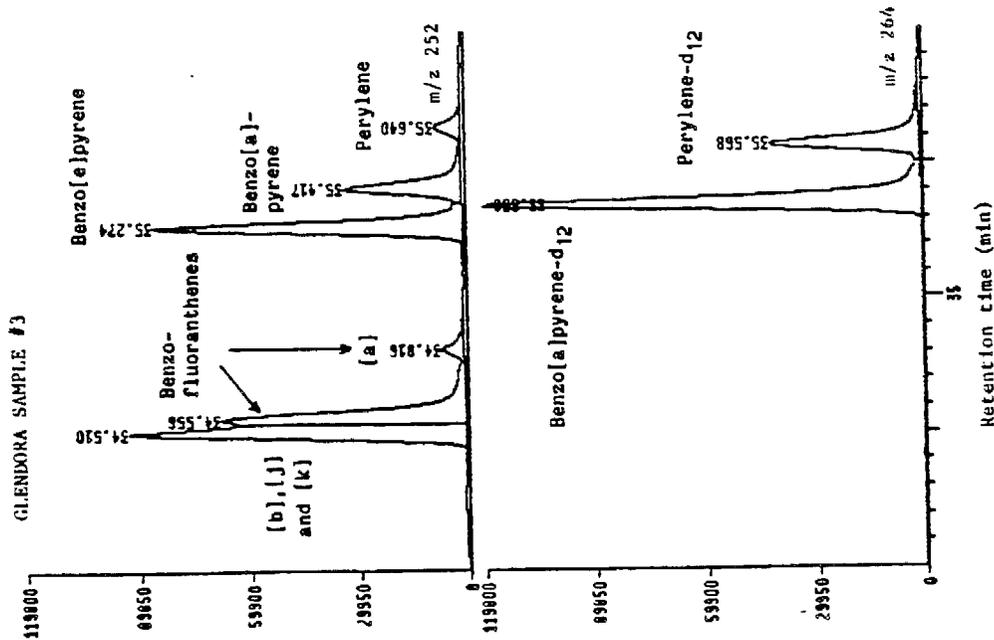
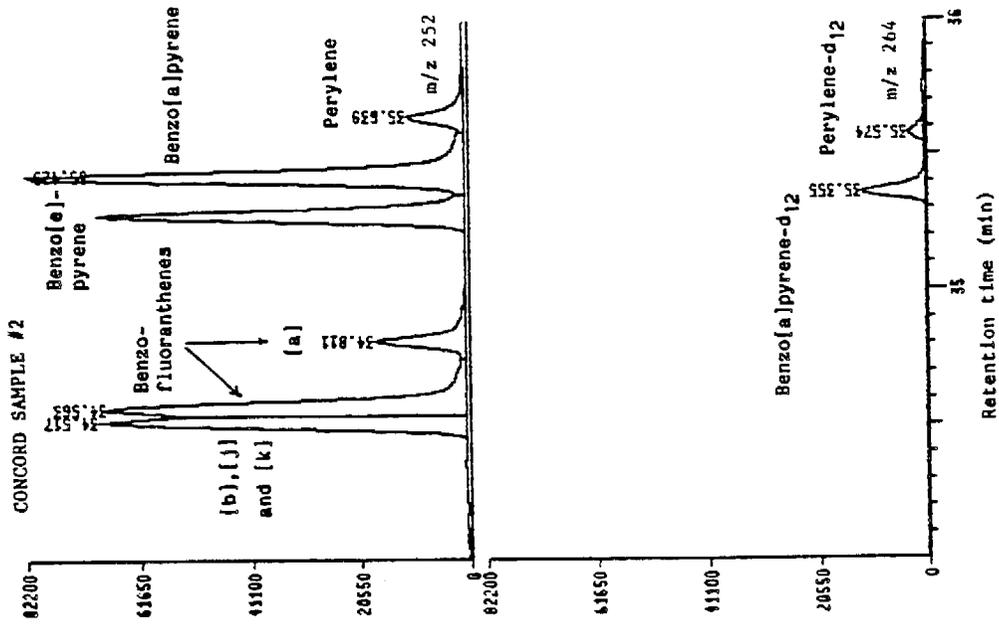


Figure VII-15. GC/MS/MID traces from the analysis of two ambient POM filter composite samples for the M.W. 252 PAH. Note that in Concord Sample #2, unlike Glendora Sample #3, benzo[a]pyrene is present in an amount similar to benzo[e]pyrene. The identification of the small peak at 34.8 min as benzo[a]fluoranthene is tentative since no standard was available.

quantification of the high M.W. species, dibenz[a,h]anthracene-d₁₄, was also distributed between these two HPLC fractions, it could not be used for quantification. In the PAH-fraction, these high M.W. PAH were quantified by ratioing their areas to that of the internal standard benzo[a]pyrene-d₁₂. For the 22-34 min HPLC fraction, chrysene-d₁₂ was added as the internal standard just prior to analyzing for the high M.W. PAH species. Since the added chrysene-d₁₂ had not been subjected to any losses inherent in the fractionation procedures, the quantifications of the high M.W. PAH in the 22-34 min HPLC fraction must be viewed as lower limits. Table C-16 (see Appendix) gives the µg quantities of the PAH of M.W. 276-300 measured in the two HPLC fractions in which they eluted. In general, the species of M.W. 276 eluted primarily in the 7-22 min HPLC fraction. The ambient concentrations given in Table VII-14 have been calculated by summing the amount in the two fractions, but must, as discussed above, be viewed as lower limits to the ambient concentrations.

Figure VII-16 gives GC/MS/MID traces of the standards of the M.W. 276 and 278 PAH. As seen from this figure, dibenz[a,c]anthracene and dibenz[a,h]anthracene co-elute and in Table VII-14, therefore, the sum of these two isomers is given. Only the indeno[1,2,3-cd]pyrene present in the 22-34 min HPLC fraction required correction for the [M-2]⁺ ion contribution of the dibenzanthracenes, since the amount of the M.W. 278 species present in the 7-22 min HPLC fraction was generally very low (see Table C-16). Benzo[ghi]perylene was the most abundant M.W. 276 PAH in all cases and was, together with coronene (M.W. 300), generally more abundant than any M.W. 278 species (Table VII-14). Due to the large number of M.W. 302 PAH (see Appendix A) and the limited number of standards available, we could not conclusively identify or quantify these PAH.

SRM 1649 Urban Particles. To validate our methods, the NBS-SRM 1649 was analyzed for PAH using the same procedures as were used for the filter composite samples. The SRM 1649 Urban Dust/Organics was collected in Washington, DC, and is available from the Office of Standard Reference Materials in 10 g units. We extracted 0.959 g of this SRM and quantified the major PAH for comparison with NBS published values (Wise et al., 1986). Table VII-15 gives the NBS reported values for the major PAH as determined by GC and/or HPLC with fluorescence detection and our values from replicate GC/MS/MID quantifications. As may be seen from this table,

Table VII-14. Lower Limit to PAH Concentrations of Targeted Species M.W. 276-300 Measured for Single or Composited Day/Night Sampling Intervals on TIGF Filters (ng m^{-3}) at the Seven Sampling Sites in California

Location Site and Dates ^A	ng m^{-3} b,c									
	Indeno-(1,2,3-od)-fluoranthene	Indeno-(1,2,3-cd)-pyrene	Benzo[ghi]-perylene	Anth-anthrene	Benzo[c]-chrycene	Dibenz[a,j]-anthracene	Dibenz[a,o]-anthracene/ Dibenz[a,h]-anthracene	Benzo[b]-chrycene	Fluorene	Coronene
Glendora 8/13/86 Sample #1 Day	0.05	0.70	1.48	0.03	0.007	0.03	0.08	0.01	0.08	0.69
Glendora 8/13-14/86 Sample #2 Night	0.16	2.78	6.09	0.26	0.02	0.10	0.22	0.03	0.06	2.41
Glendora 8/15,16,17,18/86 Sample #3A Day	0.02	0.75	1.78	e	e	0.02	0.04	e	0.02	1.98
Glendora 8/15-16,16-17, 17-18,18-19/86 Sample #4A Night	0.03	1.45	5.44	e	e	e	0.11	e	0.002	5.70
Glendora 8/20/86 Sample #5 Day	0.13	1.87	3.32	0.06	0.01	0.13	0.34	0.03	0.31	1.78
Glendora 8/20-21/86 Sample #6 Night	0.16	2.37	4.94	0.13	0.01	0.13	0.39	0.06	0.26	4.58
Yuba City 10/16,18,20/86 Sample #1 Day	0.03	0.26	0.58	e	0.004	0.01	0.03	0.005	0.03	0.19

(continued)

Table VII-14 (continued) - 2

Location Site and Dates ^a	ng m ⁻³ b,c										
	Indeno- [1,2,3-cd]- fluoranthene	Indeno- [1,2,3-cd]- pyrene	Benzo[ghi]- perylene	Anth- anthrene	Benzo[c]- chrysene	Dibenz[a,j]- anthracene	Dibenz[a,h]- anthracene	Dibenz[a,c]- anthracene/ Dibenz[a,h]- anthracene	Benzo[b]- chrysene	Fluorene	Coronene
Yuba City 10/17,23/86 Sample #2 Day	0.07	0.57	0.73	e	0.006	0.02	0.04	0.04	0.02	0.04	0.24
Yuba City 10/16-17,18-19, 20-21,23-24/86 Sample #3 Night	0.03	0.28	0.55	0.04	0.002	0.01	0.02	0.02	0.009	0.02	0.18
Concord 12/8,9/86; 1/19/87 Sample #1 Day	0.22	2.30	4.16	0.45	0.07	0.16	0.32	0.32	0.12	0.20	2.19
Concord 1/18,21,22/87 Sample #2 Day	0.30	2.65	3.72	0.46	0.13	0.21	0.39	0.39	0.16	0.33	1.17
Concord 12/6-7,7-8, 8-9/86 Sample #3 Night	0.71	5.02	5.97	2.08	0.30	0.60	1.16	1.16	0.68	1.01	2.67
Concord 1/17-18,18-19, 21-22/87 Sample #4 Night	0.75	6.24	7.67	2.22	0.30	1.93	0.91	0.91	0.58	0.89	2.40
Concord 12/10-11/86; 1/14-15/87 Sample #5 Night	0.15	1.47	2.40	0.39	0.006	0.06	0.15	0.15	0.07	0.10	0.65

(continued)

Table VII-14 (continued) - 3

Location Site and Dates ^a	ng m ⁻³ b,c									
	Indeno- (1,2,3-cd)- fluoranthene	Indeno- (1,2,3-cd)- pyrene	Benzo[ghi]- perylene	Anth- anthrene	Benzo[c]- chrysene	Dibenz[a,j]- anthracene	Dibenz[a,c]- anthracene/ Dibenz[a,h]- anthracene	Benzo[b]- chrysene	Picene	Coronene
Mammoth Lakes 2/14, 16, 17, 21, 22, 26, 28/87 Sample #1 Day	0.41	3.34	4.22	0.97	0.15	0.32	0.56	0.34	0.40	2.00
Mammoth Lakes 2/16-17, 17-18, 20-21, 27-28; 2/28-3/1/87 Sample #2 Night	2.00	12.31	11.35	3.64	0.74	2.03	3.55	2.15	2.53	6.63
Mammoth Lakes 2/14-15, 15-16, 21- 22, 22-23, 25-26/87 Sample #3 Night	0.45	2.85	2.95	0.83	0.16	0.43	0.78	0.47	0.57	1.63
Oildale 3/30, 31/87; 4/1, 2, 7, 8, 9, 10/87 Sample #1 Day	0.03	0.50	0.67	0.04	0.01	0.08	0.14	0.07	0.31	0.25
Oildale 3/29-30/87; 4/9-10, 10-11/87 Sample #2 Night	0.01	0.17	0.32	e	e	0.006	0.02	0.01	0.05	0.13
Oildale 3/31-4/1/87; 4/1-2, 7-8, 8-9/87 Sample #3 Night	0.04	0.81	1.14	0.03	0.02	0.10	0.08	0.07	0.31	0.21

(continued)

Table VII-14 (continued) - 4

Location Site and Dates ^a	ng m ⁻³ b,c									
	Indeno- [1,2,3-cd]- fluoranthene	Indeno- [1,2,3-cd]- pyrene	Benzo[ghi]- perylene	Anth- anthrene	Benzo[c]- chrysene	Dibenz[a,j]- anthracene	Dibenz[a,c]- anthracene/ Dibenz[a,h]- anthracene	Benzo[b]- chrysene	Picene	Coronene
Reseda 5/28,29,30,31/87; 6/1,2,14,15/87 Sample #1 Day	0.05	0.61	1.40	0.08	0.02	0.04	0.08	0.03	0.05	0.73
Reseda 5/27-28,28-29, 29-30,30-31,5/31- 6/1;6/1-2,2-3, 13-14,14-15/87 Sample #2 Night ^f	0.01	0.11	0.23	0.005	0.005	0.004	0.008	e	0.004	e
Pt. Arguello 7/4,5,6,7,8,9, 10,11,12/87 Sample #1 Day	e	e	e	e	e	e	e	e	e	e
Pt. Arguello 7/4-5,5-6,6-7, 7-8,8-9,9-10, 10-11,11-12/87 Sample #2 Night	e	e	0.002	e	e	e	e	e	e	e

^aSee Section V for full details of compositing.

^bAverage of replicate GC/MS injections.

^cAmounts present in two HPLC fractions (7-22 min and 22-34 min) have been summed (see text for details).

^dCompounds co-elute, therefore, concentration given is their sum.

^eNone detected or present in trace amounts too low to quantify.

^fOnly amounts present in the 7-22 min HPLC fraction were used to calculate the concentrations since the replicate values for the 22-34 min HPLC fraction were not in agreement (see Table C-16).

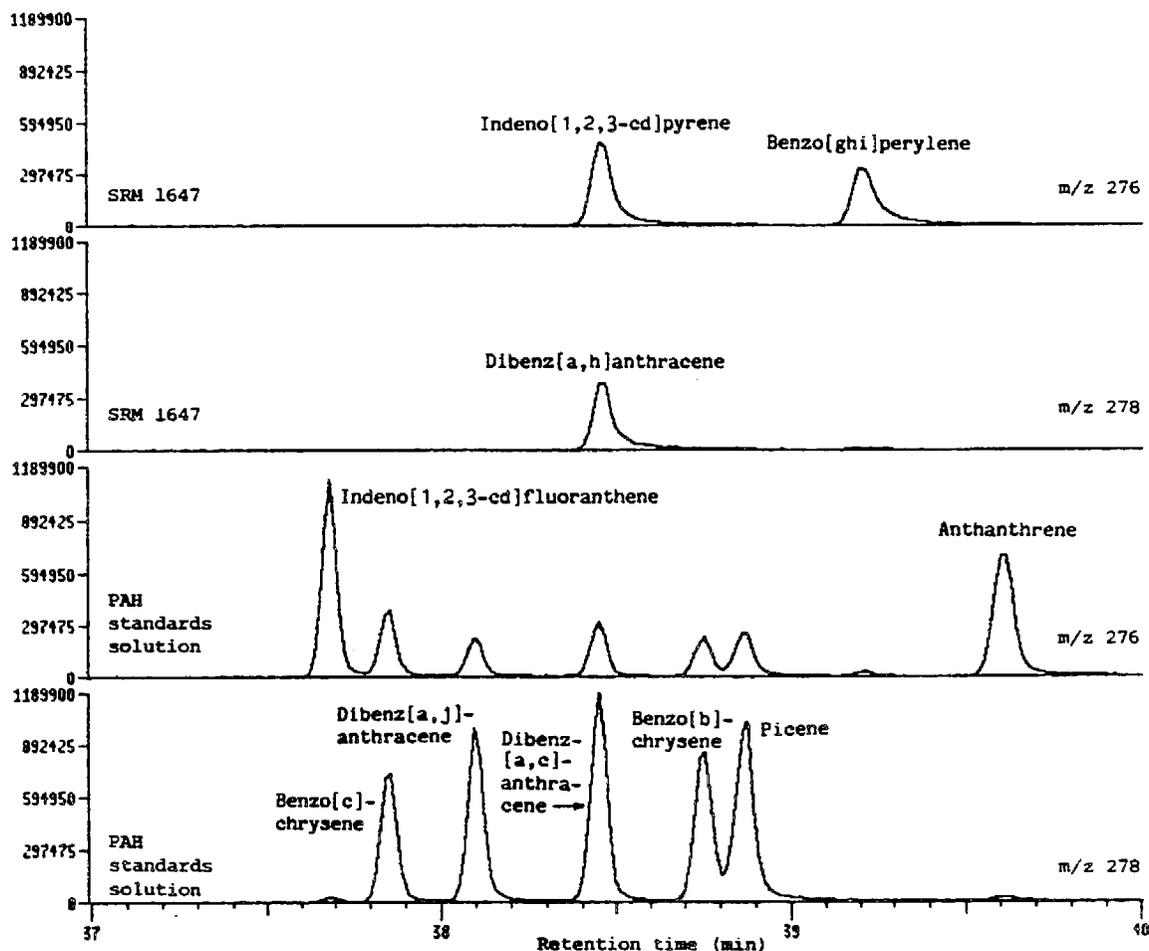


Figure VII-16. MID traces from the GC/MS/MID analyses of the SRM 1647 standard PAH solution (spiked with deuterated internal standards) and a standard solution consisting of the deuterated internal standards and those PAH to be monitored which were not present in the SRM. The internal standard dibenz[a,h]anthracene- d_{14} is not shown. It can be seen that dibenz[a,c]anthracene and dibenz[a,h]anthracene (M.W. 278) co-elute and their sum is reported in Table VII-14. The indeno[1,2,3-cd]pyrene peak area was corrected, as necessary, for the contribution of the $[M-2]^+$ peak of dibenz[a,h]anthracene/dibenz[a,c]anthracene (see text for details).

Table VII-15. PAH in NBS Standard Reference Material 1649, Washington, D.C. Air Particulate Sample

PAH	$\mu\text{g g}^{-1}$		SAPRC Values for Replicate GC/MS Analysis
	NBS Values ^a		
	GC	LC	
Fluoranthene	7.3 ± 0.2	7.1 ± 0.5	7.8, 7.9
Pyrene	7.2 ± 0.2	6.0 ± 0.2	6.9, 6.8
Benz[a]anthracene	2.4 ± 0.1	2.4 ± 0.1	3.5, 3.4
Chrysene	} 4.6 ± 0.2	3.5 ± 0.1	} 7.0, 6.9
Triphenylene		1.7 ± 0.1	
Benzo[b]fluoranthene	-	6.0 ± 0.3	-
Benzo[k]fluoranthene	-	2.0 ± 0.1	-
Σ Benzofluoranthenes [b, j and k isomers]	-	-	10.8, 10.4
Benzo[e]pyrene	3.3 ± 0.2	3.9 ± 0.3	4.4, 4.3
Benzo[a]pyrene	3.0 ± 0.3	2.4 ± 0.2	3.3, 3.1
Perylene	0.84 ± 0.09	0.74 ± 0.05	0.96, 0.86
Indeno[1,2,3-cd]pyrene	3.3 ± 0.3	3.4 ± 0.1	6.2, ^b 6.0 ^b
Benzo[ghi]perylene	4.7 ± 0.2	4.1 ± 0.1	12.5, ^c 12.3 ^c
Dibenz[a,h]anthracene	-	0.45 ± 0.04	
Σ Dibenzanthracene [a,h and a,c isomers]			0.56, ^d 0.40 ^d

^aWise et al. (1986).

^bPresent in two HPLC fractions as follows ($\mu\text{g g}^{-1}$): [7-22 min] 2.3, 2.1; [22-34 min] 3.9, 3.9.

^cPresent in two HPLC fractions as follows ($\mu\text{g g}^{-1}$): [7-22 min] 4.1, 4.0; [22-34 min] 8.4, 8.3.

^dPresent in two HPLC fractions as follows ($\mu\text{g g}^{-1}$): [7-22 min] 0.15, not quantified; [22-34 min] 0.41, 0.40.

agreement is generally excellent for the PAH which elute entirely in the 7-22 min HPLC fraction (see Scheme VI-1), i.e. from M.W. 202-252. For the heavier PAH which eluted in two HPLC fractions, up to a factor of three disagreement exists. Unlike most of the composite samples analyzed, the SRM analysis had a large fraction of the M.W. 276 species present in the second HPLC fraction. The reasons for this and for our disagreement with the NBS values is unknown, but certainly the ambient concentrations of the high M.W. PAH given in Table VII-14 must be viewed as being significantly more uncertain than those of the lower M.W. PAH.

Nitroarenes Sampled on TIGF Filters. As expected, the nitroarenes were less abundant than their parent PAH and were not the major constituents of the HPLC fraction in which they were eluted. Since the nitrofluoranthenes and nitropyrenes were expected to be the most abundant particle-associated nitroarenes, and furthermore, provide information on the atmospheric transformation of the PAH (see Section IX), we concentrated first on quantifying these species. The ambient concentrations of 2- and 8-nitrofluoranthene and 1- and 2-nitropyrene and the observation of 3-nitrofluoranthene for twenty-five composite filter samples are given in Table VII-16.

Figure VII-17 gives GC/MS/MID traces showing the separation of the five nitrofluoranthenes and three nitropyrenes on the GC column used, and of the standard solution used for external calibration of those isomers for which deuterated internal standards were not added. As discussed in Section VI-C, 90% of the 22-34 min fraction from the normal-phase HPLC separation was fractionated further by reverse-phase HPLC to isolate the nitroarenes of M.W. 247. For the Concord and Mammoth Lakes samples which contained high levels of PAH, the second HPLC fractionation was not sufficient to allow us to unequivocally identify and quantify the nitrofluoranthenes and nitropyrenes (see left sides of Figures VII-18 and VII-19). Indeed, in the analysis of Mammoth Lakes Sample #2 (Figure VII-19), the deuterated internal standards were only clearly identified from their fragment ion peaks rather than the molecular ions. A third HPLC fractionation, returning to the normal phase column with isocratic elution, was performed on the Concord and Mammoth Lakes samples (Section VI-C) prior to GC/MS quantification.

Table VII-16. Nitrofluoranthene and Nitropyrene Concentrations Measured for Single or Compositd Day/Night Sampling Intervals on TIGF Filters (pg m⁻³) at the Seven Sites in California and at San Nicolas Island

Location Site and Dates ^a	Day/Night	pg m ⁻³ b				
		2-Nitro-fluoranthene	3-Nitro-fluoranthene	8-Nitro-fluoranthene	1-Nitro-pyrene	2-Nitro-pyrene
Glendora 8/13/86	Sample #1 Day	210	c	3.9	26	16
Glendora 8/13-14/86	Sample #2 Night	500	c	8.6	37	53
Glendora 8/15, 16, 17, 18/86	Sample #3A ^d Day	240	e	2.3	11	6.4
Glendora 8/15-16, 16-17, 17-18, 18-19/86	Sample #4A ^d Night	870	c	3.4	14	21
Glendora 8/20/86	Sample #5 Day	350	c	3.1	15	14
Glendora 8/20-21/86	Sample #6 Night	2,000	c	3.7	15	32
Yuba City 10/16, 18, 20/86	Sample #1 Day	52	e	0.83	6.8	3.2
Yuba City 10/17, 23/86	Sample #2 Day	250	c	2.7	14	17
Yuba City 10/16-17, 18-19, 20-21, 23-24/86	Sample #3 Night	150	c	1.3	6.0	9.2
Concord 12/8, 9/86; 1/19/87	Sample #1 ^f Day	140	e	3.2	26	30

(continued)

Table VII-16 (continued) - 2

Location Site and Dates ^a		pg m ⁻³ b					
		2-Nitro-fluoranthene	3-Nitro-fluoranthene	8-Nitro-fluoranthene	1-Nitro-pyrene	2-Nitro-pyrene	
Concord	Sample #2 ^f 1/18,21,22/87	Day	500	c	3.7	19	56
Concord	Sample #3 ^f 12/6-7,7-8,8-9/86	Night	220	c	10 ^g	41 ^g	50 ^g
Concord	Sample #4 ^f 1/17-18,18-19,21-22/87	Night	380	c	14 ^g	45 ^g	81 ^g
Concord	Sample #5 ^f 12/10-11/86; 1/14-15/87	Night	130	c	2.2	14	19
Mammoth Lakes	Sample #1 ^f 2/14,16,17,21,22,26,28/87	Day	17	c	h	8.3	3.0
Mammoth Lakes	Sample #2 ^f 2/16-17,17-18,20-21,27-28;2/28-3/1/87	Night	58 ^g	c	h	h	h
Mammoth Lakes	Sample #3 ^f 2/14-15,15-16,21-22,22-23,25-26/87	Night	14 ^g	c	h	h	h
Oildale	Sample #1 3/30,31/87; 4/1,2,7,8,9,10/87	Day	22	c	0.13	5.3	1.0
Oildale	Sample #2 3/29-30/87; 4/9-10,10-11/87	Night	35	c	c	4.9	1.0
Oildale	Sample #3 3/31-4/1/87; 4/1-2,7-8,8-9/87	Night	37	c	c	11	1.5
Reseda	Sample #1 5/28,29,30,31/87; 6/1,2,14,15/87	Day	240	c	2.1	11	21

(continued)

Table VII-16 (continued) - 3

Location Site and Dates ^a		pg m ⁻³ b				
		2-Nitro-fluoranthene	3-Nitro-fluoranthene	8-Nitro-fluoranthene	1-Nitro-pyrene	2-Nitro-pyrene
Reseda	Sample #2	78	c	0.71	5.4	5.6
5/27-28, 28-29, 29-30, 30-31, 5/31-6/1; 6/1-2, 2-3, 13-14, 14-15/87	Night					
	Sample #1	3.5	c	c	0.65	0.29
Pt. Arguello	Sample #1	Day				
7/4, 5, 6, 7, 8, 9, 10, 11, 12/87	Day					
Pt. Arguello	Sample #2	5.6	c	c	0.33	c
7/4-5, 5-6, 6-7, 7-8, 8-9, 9-10, 10-11, 11-12/87	Night					
San Nicolas Island	Composite	1.8	c	c	0.28	c
6/19-20, 24-26; 7/13-16; 8/27-30; 9/2-4/87	Composite					

^aSee Section V for full details of compositing.

^bAverage of replicate injections.

^cNone detected.

^dExtracted with CH₂Cl₂, see Section VI for details.

^ePresent in an amount too small to quantify.

^fThree HPLC fractionations performed to isolate the nitrofluoranthenes and nitropyrenes.

^gQuantified on the response of the [M-NO₂]⁺ fragment ion due to interference or high background in the [M]⁺ ion trace.

^hBackground interferences too high to allow positive identification of nitroarene peaks.

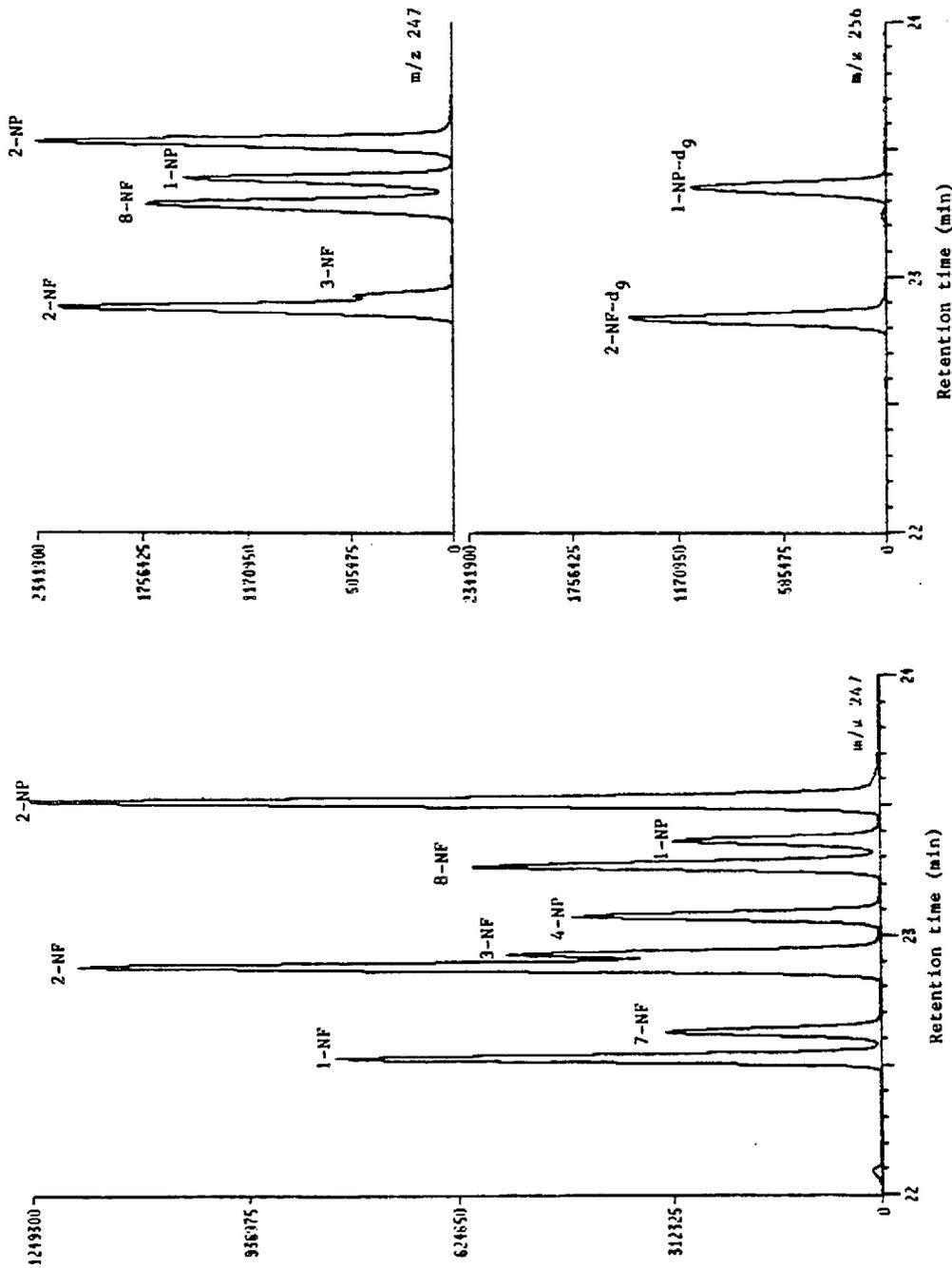


Figure VII-17. GC/MS/MID trace showing the molecular ion (m/z 247) of a solution of the nitrofluoranthene (NF) and nitropyrenes (NP) [left]. Note that all but 2- and 3-nitrofluoranthene are baseline resolved. GC/MS/MID traces of the molecular ions for a standard solution with deuterated internal standards are shown on the right. This solution was utilized for external calibration of 3-NF, 8-NF and 2-NP and contained ($\text{ng } \mu\text{L}^{-1}$): 2-NF-d₉, 21.4; 1-NP-d₉, 20.0; 2-NF, 19.2; 3-NF, 4.7; 8-NF, 22.5; 1-NP, 20.5; 2-NP, 22.0.

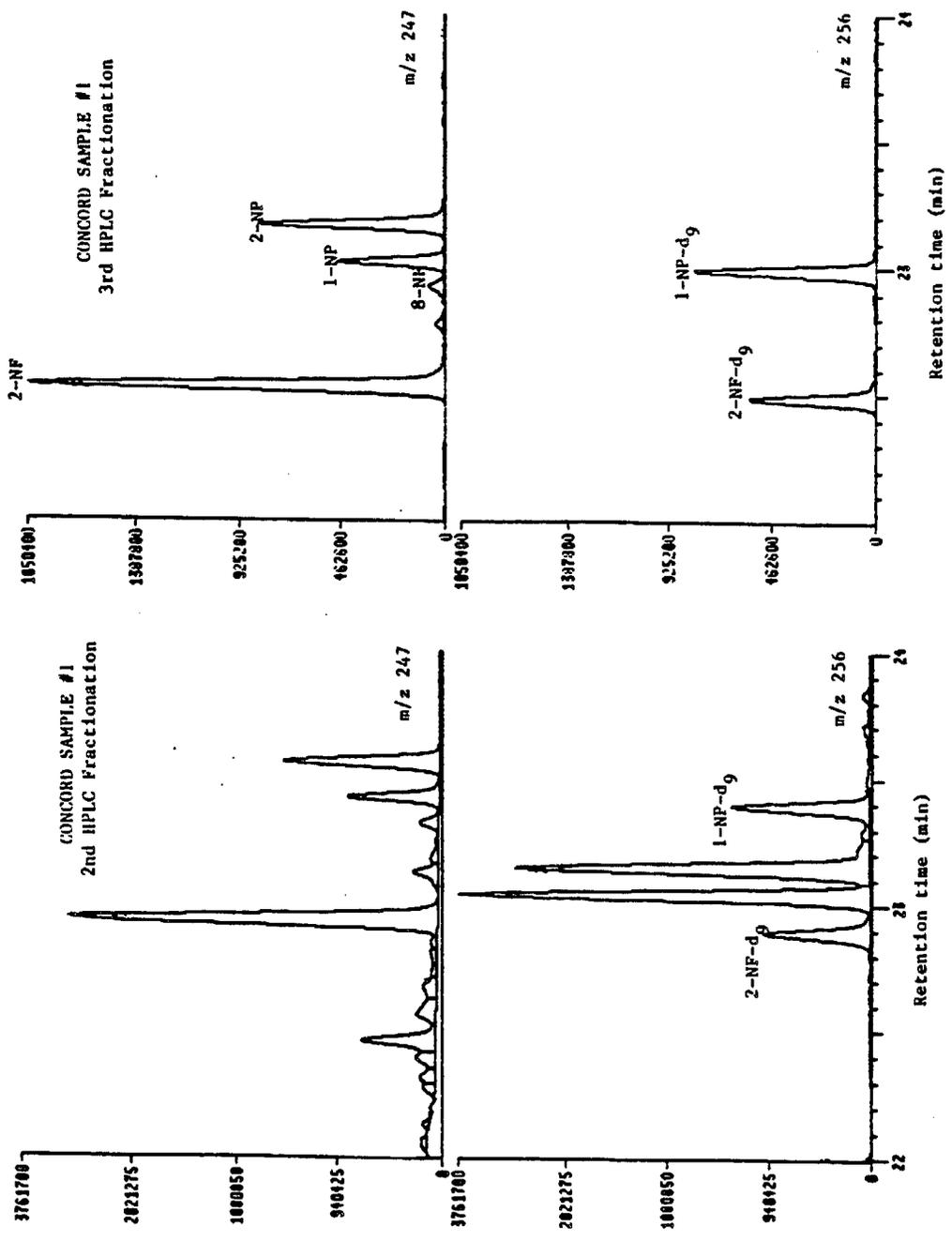


Figure VII-18. GC/MS/MID traces from the analysis of Concord Sample #1 for the M.W. 247 nitroarenes after two HPLC fractionation steps (left) and after a third HPLC fractionation (right). Note that several interfering peaks were removed by the third fractionation making the deuterated standard and the nitrofluoroanthene (NF) and nitropyrene (NP) molecular ion peaks readily quantifiable. The retention times are slightly shorter for the GC/MS analysis of the third fractionation since the column was shortened (and the inlet cleaned) when peak-tailing began to occur.

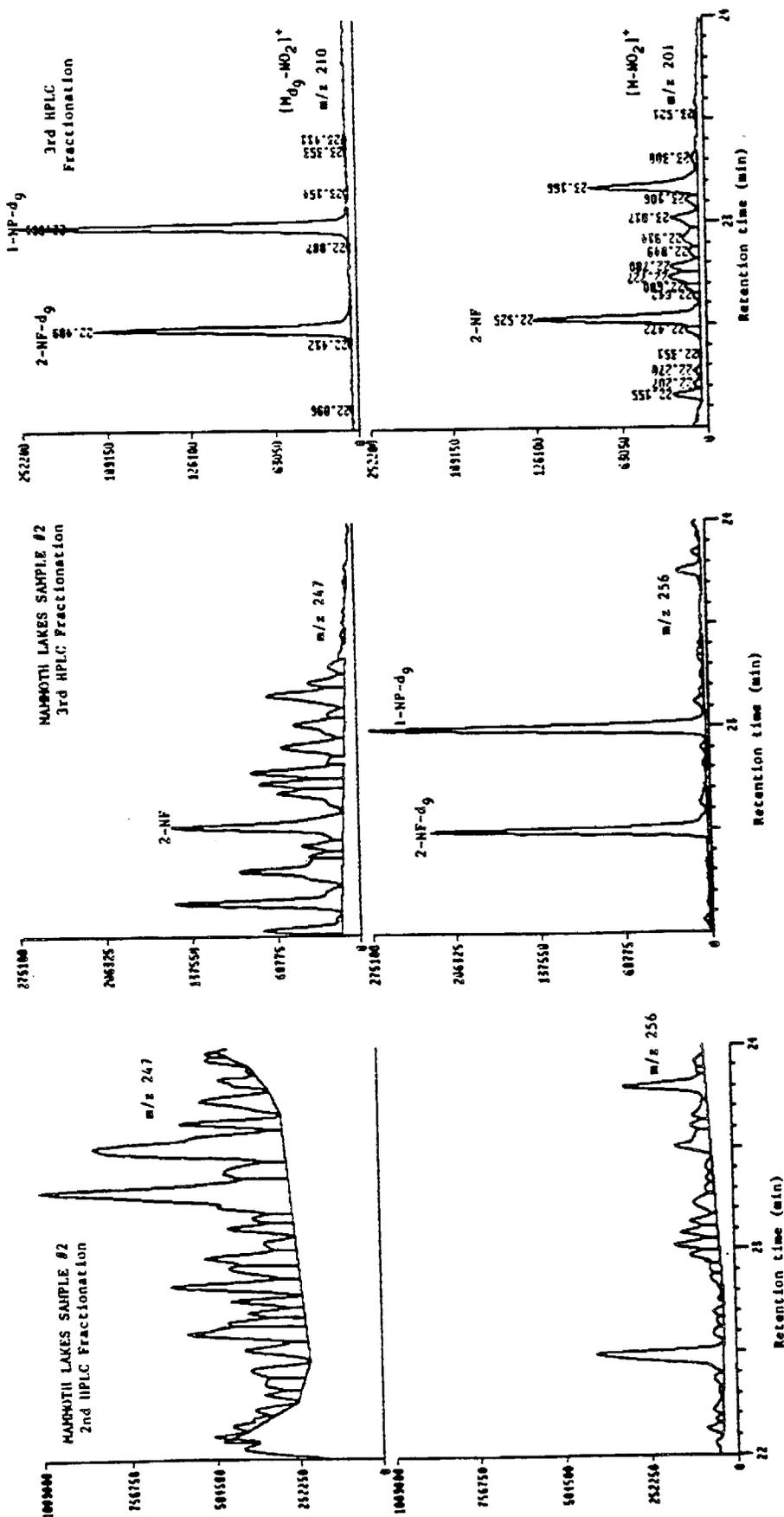


Figure VII-19. GC/MS/MID traces from the analysis of Mammoth Lakes Sample #2 for the M.W. 247 nitro-arenes after two HPLC fractionation steps (left) and after a third HPLC fractionation (center and right). After two HPLC fractionations, the molecular ion peaks of the deuterated internal standards were not well resolved from interfering peaks and the background for the m/z 247 ion obscured any nitrofluoranthene (NF) or nitropyrene (NP) peaks. Following the third HPLC fractionation, the molecular ion peaks of the deuterated internal standards (m/z 256; center) were apparent and a peak (m/z 247) eluting just after the 2-NF-d₉ standard was assigned to 2-NF. This peak was present for the fragment ions monitored, as well as the molecular ion, supporting the assignment of 2-NF. Since the [M-NO₂]⁺ fragment ion peak was judged to have been integrated more accurately (see right), 2-NF was quantified on the basis of this fragment ion.

The ambient concentrations of the M.W. 247 nitroarenes at Concord were second only to those observed at Glendora (Table VII-16) and, as seen from Figure VII-18, could be readily quantified after the third HPLC fractionation. As seen from Figure VII-19, after a third HPLC fractionation of the Mammoth Lakes Sample #2 the deuterated standards were well resolved and 2-nitrofluoranthene could be quantified on the basis on the $[M-NO_2]^+$ fragment ion. Positive identification of 1- and 2-nitropyrene in Mammoth Lakes Sample #2 was not possible even after three HPLC fractionations.

As seen from Table VII-16 and Figures VII-20 through VII-34, which give the molecular ion traces from GC/MS/MID analyses for the M.W. 247 nitroarenes, 2-nitrofluoranthene was the most abundant nitroarene of M.W. 247 in each of the twenty-five composite filter samples. The atmospheric formation of 2-nitrofluoranthene and 2-nitropyrene is discussed in Section IX and the contribution of these M.W. 247 nitroarenes to the ambient mutagenicity at the seven sampling sites is given in Section X.

Traces of 9-nitroanthracene were observed in the Glendora PUF plug samples (Final Report to ARB Contract No. A5-150-32), with more expected to be present in the filters samples. Thus, although it was not among the nitroarenes targeted for monitoring, we quantified this nitroarene once a deuterated standard had been synthesized. The ambient concentrations of 9-nitroanthracene are given in Table VII-17, together with the 1- and 2-nitronaphthalene observed in the filter samples (most of the nitronaphthalenes were observed in the PUF plug extracts). The concentration values given for the Glendora samples and Yuba City Sample #1 must be regarded as lower limits since the 9-nitroanthracene- d_9 internal standard was added after the HPLC fractionation and, therefore, losses during the fractionation have not been taken into account. Interestingly, for two of the Concord nighttime composite samples the 9-nitroanthracene concentrations were somewhat greater than the 2-nitrofluoranthene concentrations, being 330 vs. 220 $ng\ m^{-3}$ and 660 vs. 380 $ng\ m^{-3}$ for 9-nitroanthracene vs. 2-nitrofluoranthene in Concord Samples #3 and #4, respectively. However, 9-nitroanthracene will not contribute significantly to the direct-acting ambient POM mutagenicity of these Concord samples, since the specific activity of 9-nitroanthracene (strain TA98, -S9) is only 0.3 $rev\ \mu g^{-1}$ (Pitts et al. 1982b) [while the corresponding activity for 2-nitrofluoranthene is 4200 $rev\ \mu g^{-1}$].

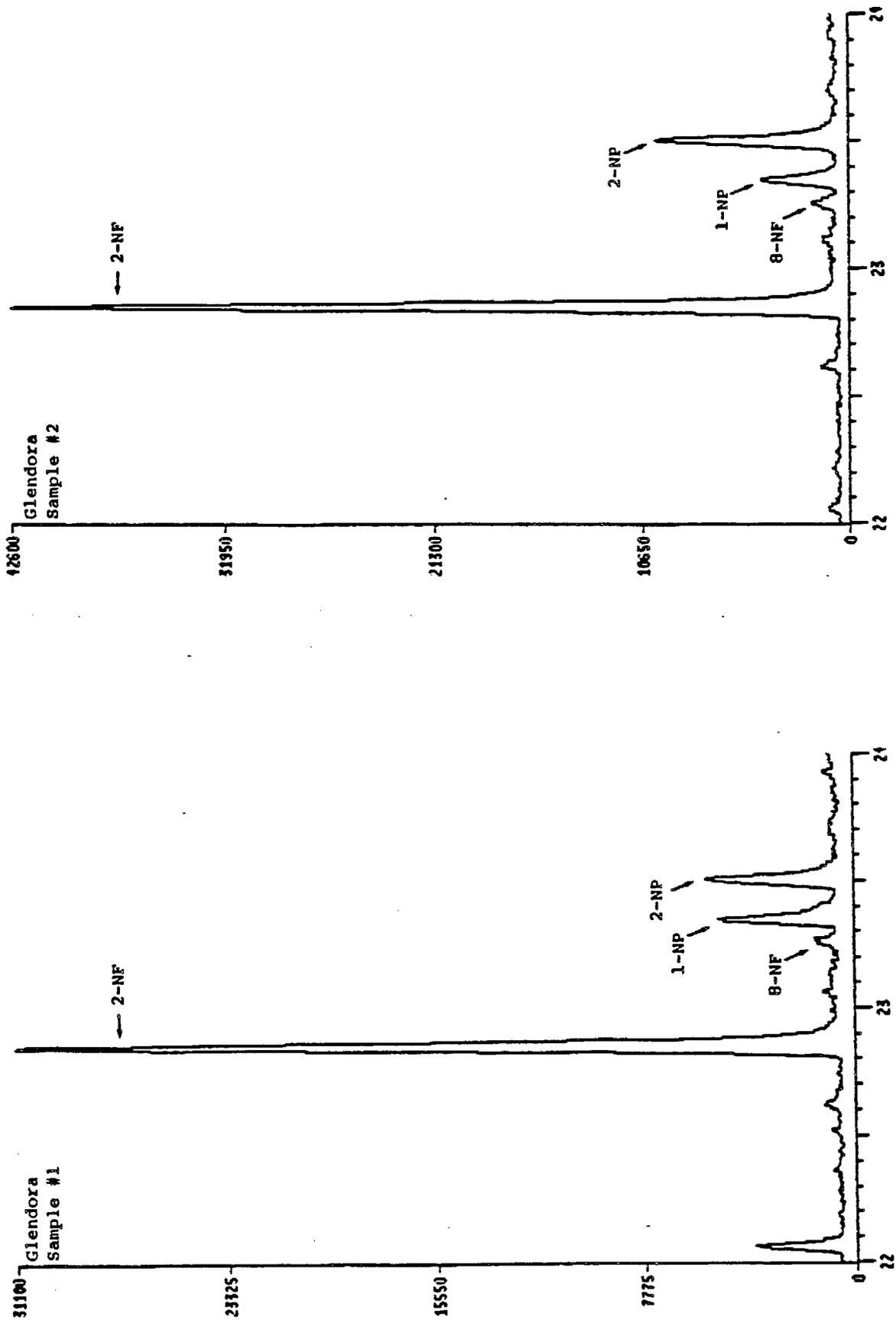


Figure VII-20. GC/MS/MID traces of the molecular ion (m/z 247) of the nitrofluoranthenes (NF) and nitro-pyrenes (NP) in Glendora filter composites, Samples #1 and #2.

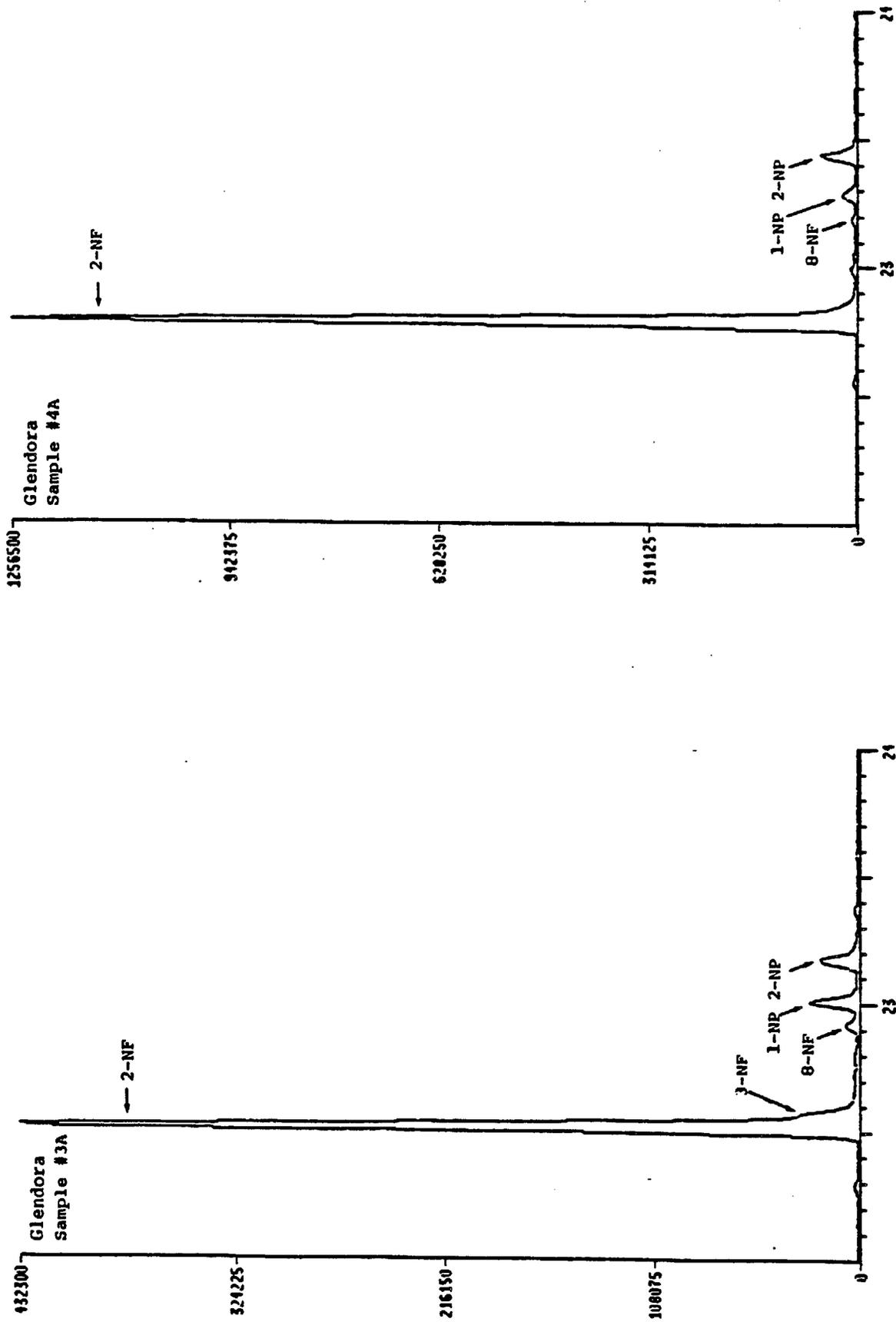


Figure VII-21. GC/MS/MID traces of the molecular ion (m/z 247) of the nitrofluoranthenes (NF) and nitro-pyrenes (NP) in Glendora filter composites, Samples #3A and #4A.

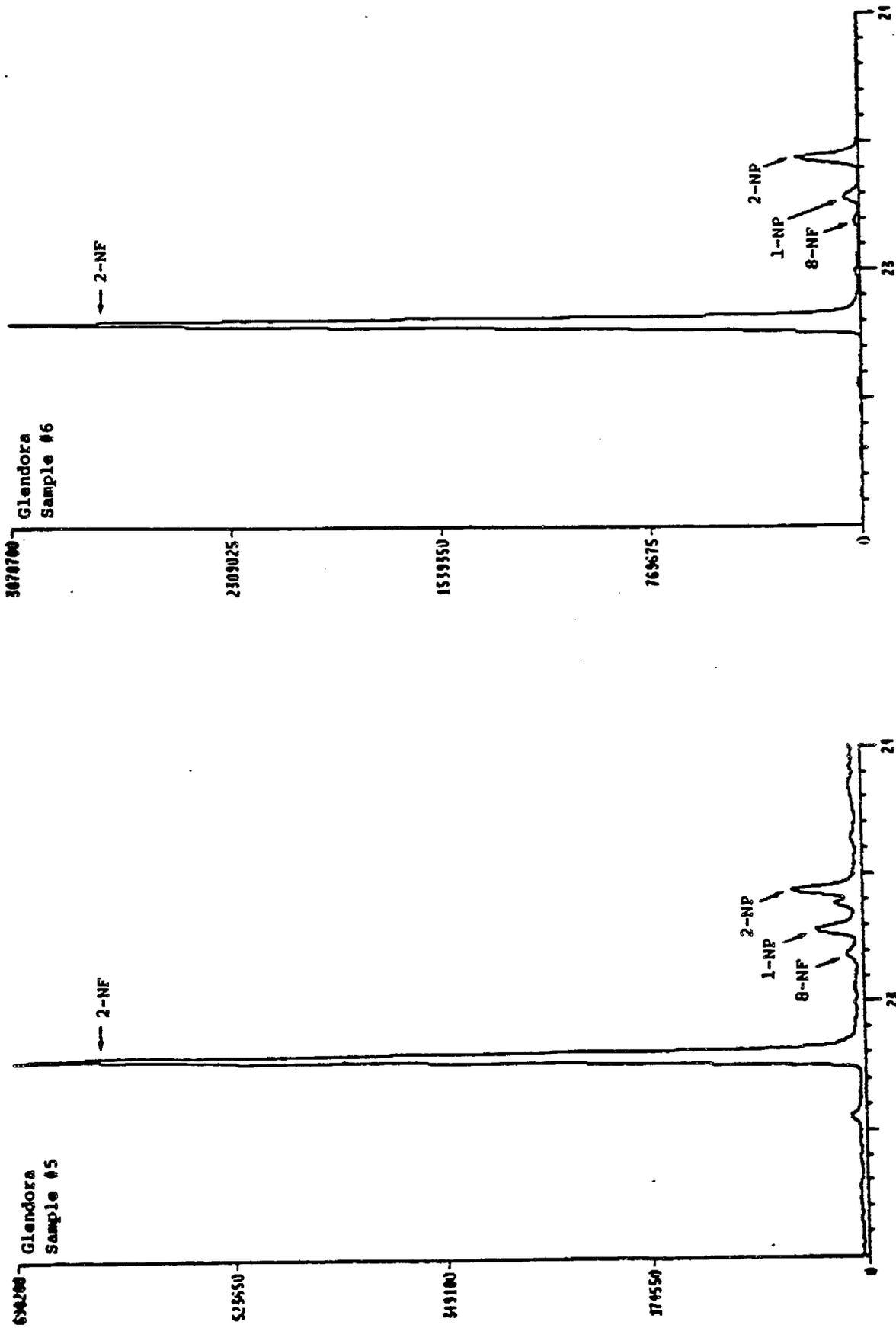


Figure VII-22. GC/MS/MID traces of the molecular ion (m/z 247) of the nitrofluoranthenes (NF) and nitro-pyrenes (NP) in Glendora filter composites, Samples #5 and #6.

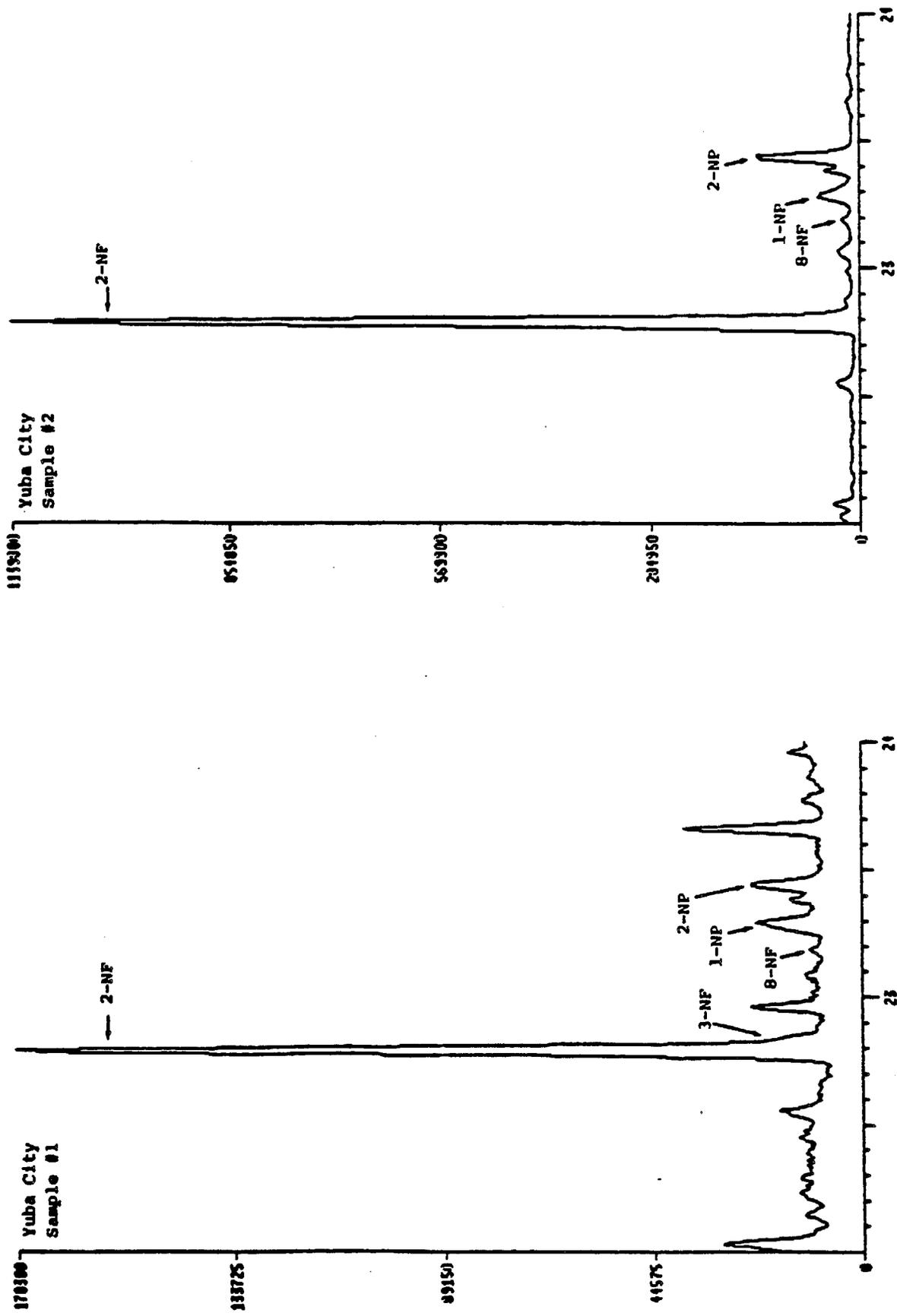


Figure VII-23. GC/MS/MID traces of the molecular ion (m/z 247) of the nitrofluoranthenes (NF) and nitro-pyrenes (NP) in Yuba City filter composites, Samples #1 and #2.

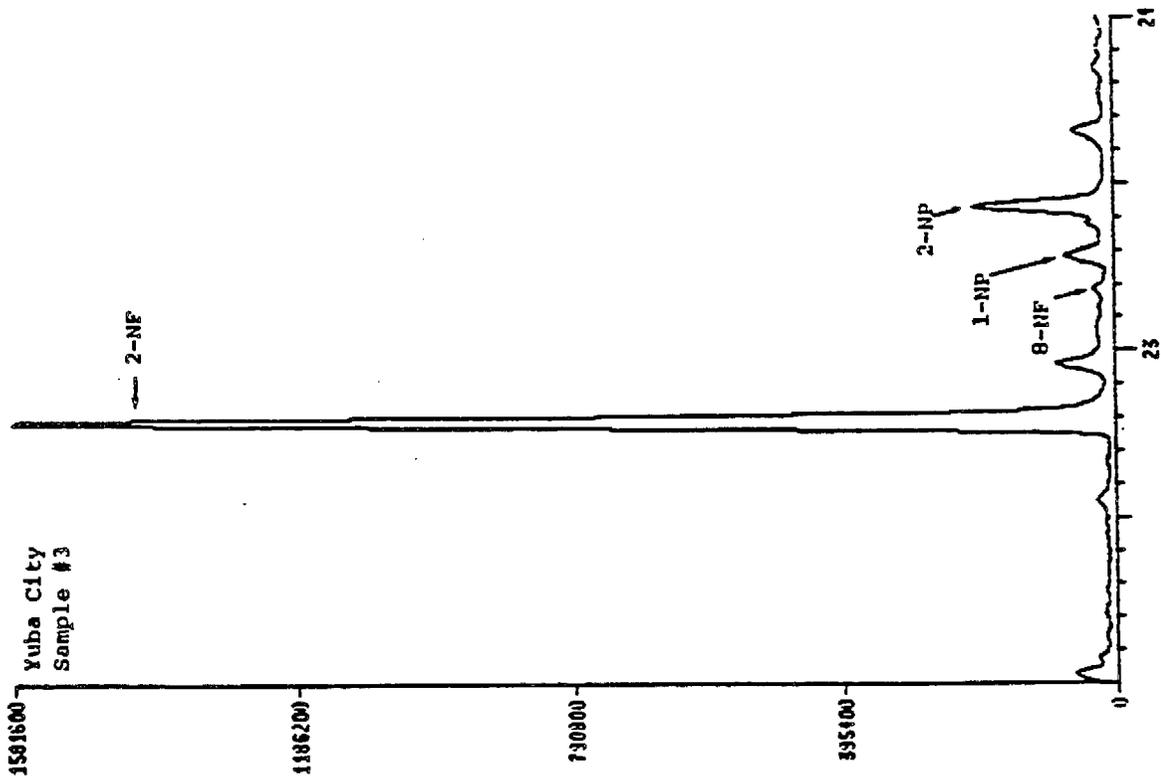


Figure VII-24. GC/MS/MID trace of the molecular ion (m/z 247) of the nitrofluoranthenes (NF) and nitropyrenes (NP) in Yuba City filter composite, Sample #3.

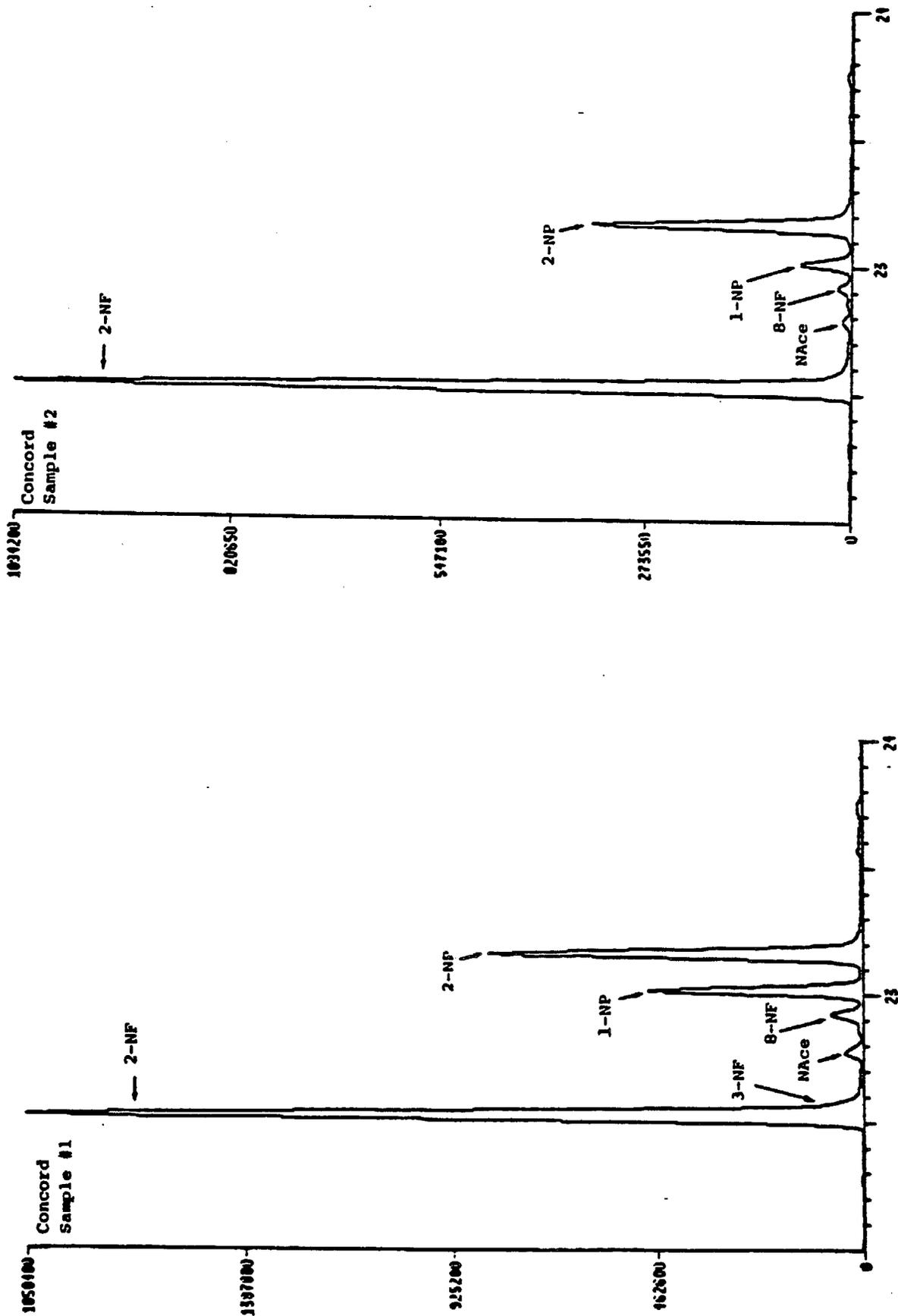


Figure VII-25. GC/MS/MID traces of the molecular ion (m/z 247) of the nitrofluoranthenes (NF), nitro-pyrenes (NP) and nitroacephenanthrylenes (NAcE) in Concord filter composites, Samples #1 and #2.

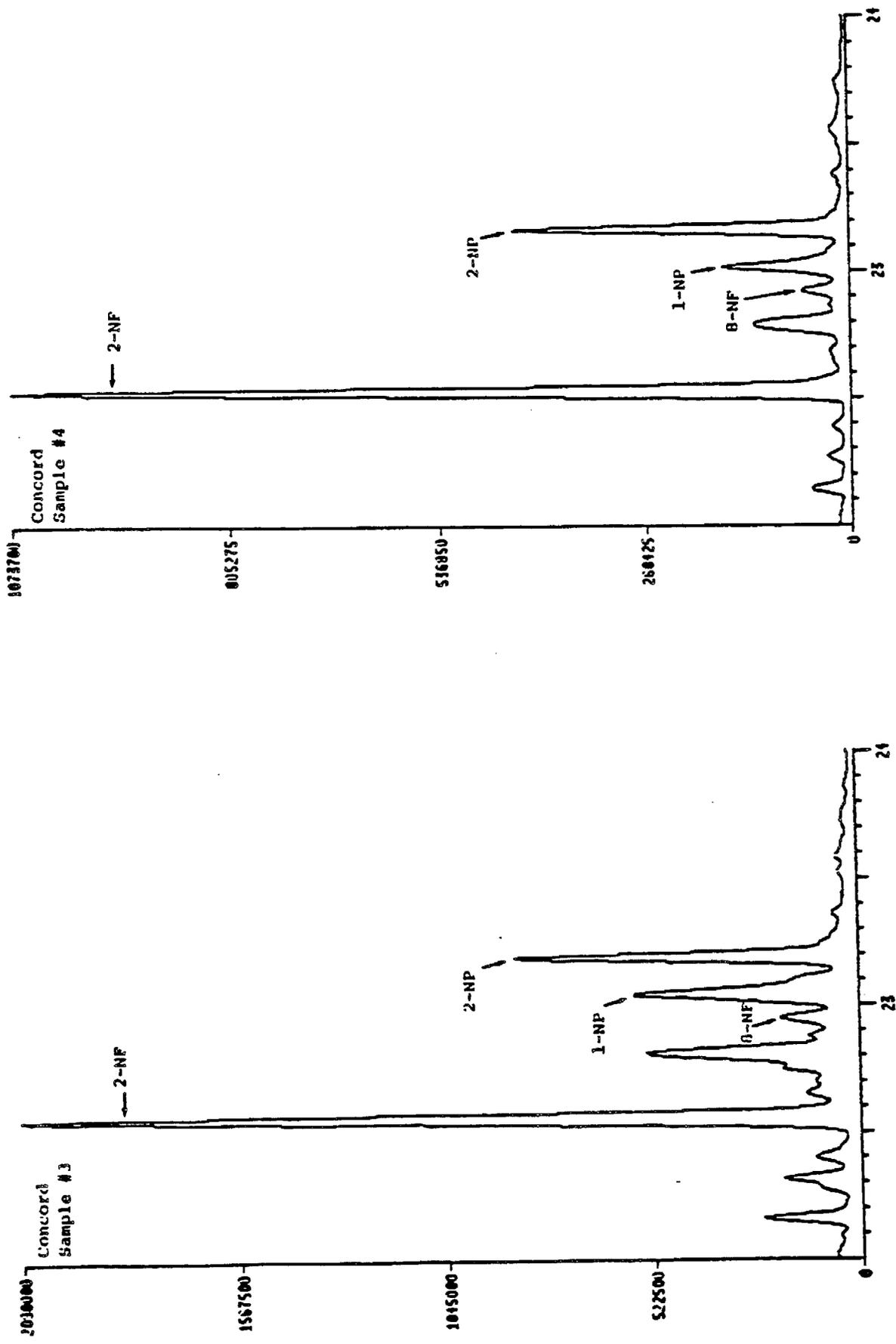


Figure VII-26. GC/MS/MID traces of the molecular ion (m/z 247) of the nitrofluoranthenes (NF) and nitro-pyrenes (NP) in Concord filter composites, Samples #3 and #4. Note that although three HPLC fractionations were performed on the Concord extracts, interferences still remained and, therefore, the presence of a nitroacephenanthrylene isomer could not be confirmed and the 1-NP and 2-NP present in these samples were quantified using the $[M-NO_2]^+$ fragment ion peak (see Table VII-16).

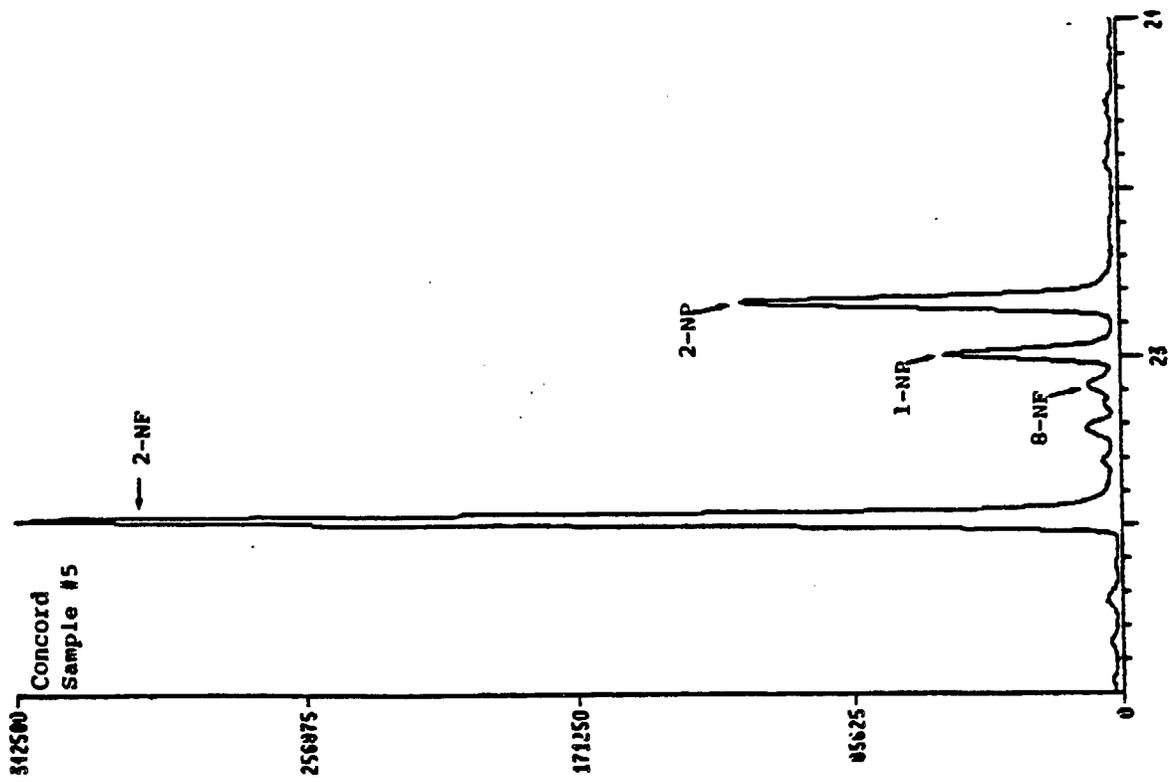


Figure VII-27. GC/MS/MID trace of the molecular ion (m/z 247) of the nitrofluoranthenes (NF) and nitropyrenes (NP) in Concord filter composite, Sample #5.

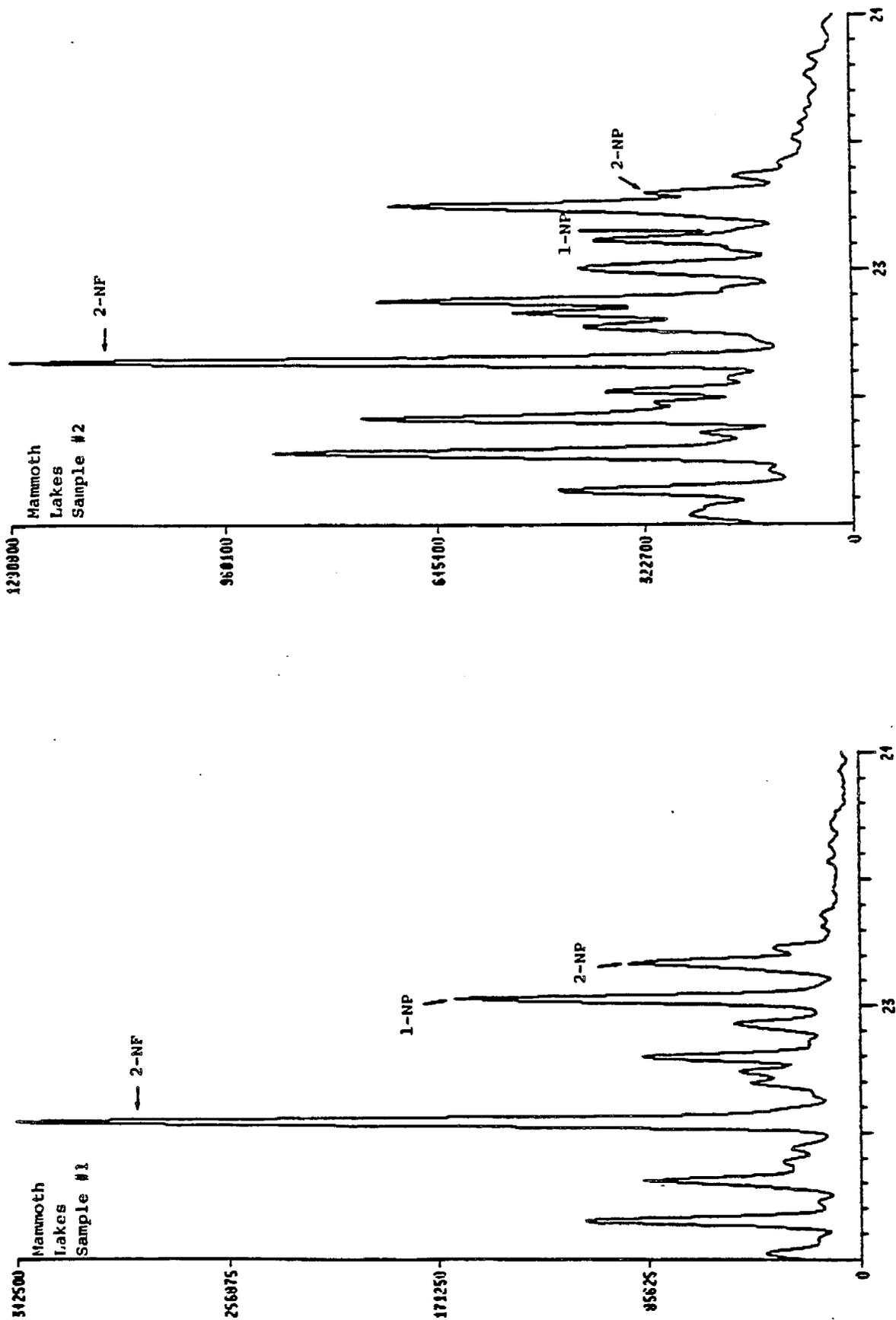


Figure VII-28. GC/MS/MID traces of the molecular ions (m/z 247) of the nitrofluoranthenes (NF) and nitropyrenes (NP) in Mammoth Lakes filter composites, Samples #1 and #2. Note that although three HPLC fractionations were performed on the Mammoth Lakes samples, interferences still remained in the molecular ion traces. See Figure VII-19 and Table VII-16 for further details.

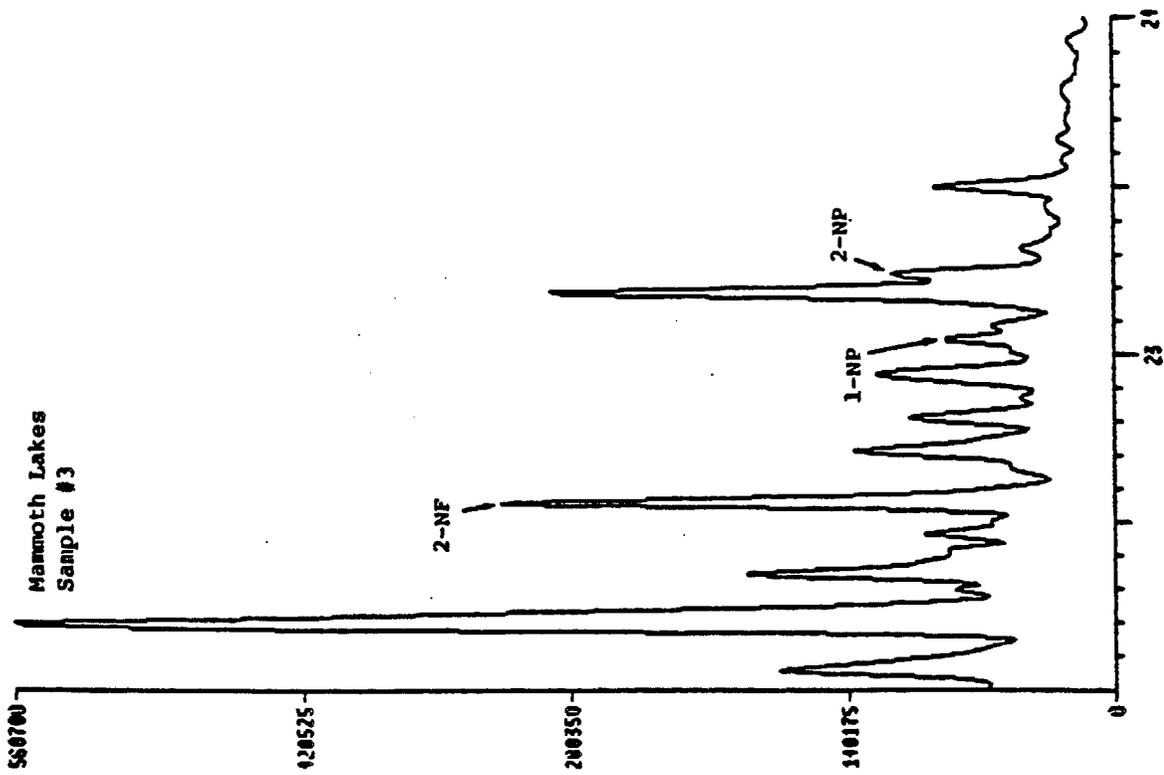


Figure VII-29. GC/MS/MID trace of the molecular ions (m/z 247) of the nitrofluoranthenes (NF) and nitro-pyrenes (NP) in Mammoth Lakes filter composite, Sample #3. Note that although three HPLC fractionations were performed on the Mammoth Lakes samples, interferences still remained in the molecular ion traces. See Figure VII-19 and Table VII-16 for further details.

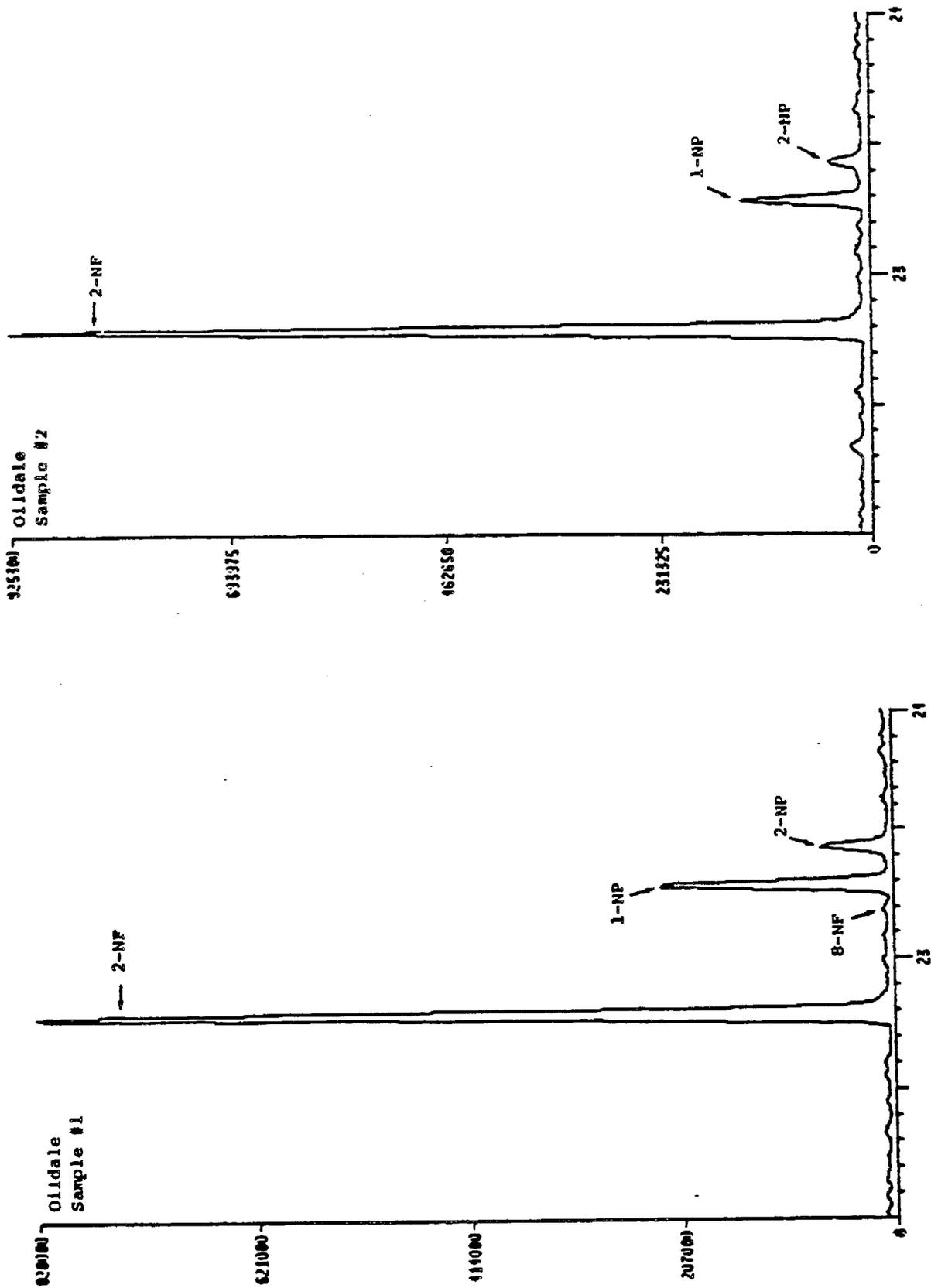


Figure VII-30. GC/MS/MID traces of the molecular ions (m/z 247) of the nitrofluoranthenes (NF) and nitropyrenes (NP) in Oildale filter composites, Samples #1 and #2.

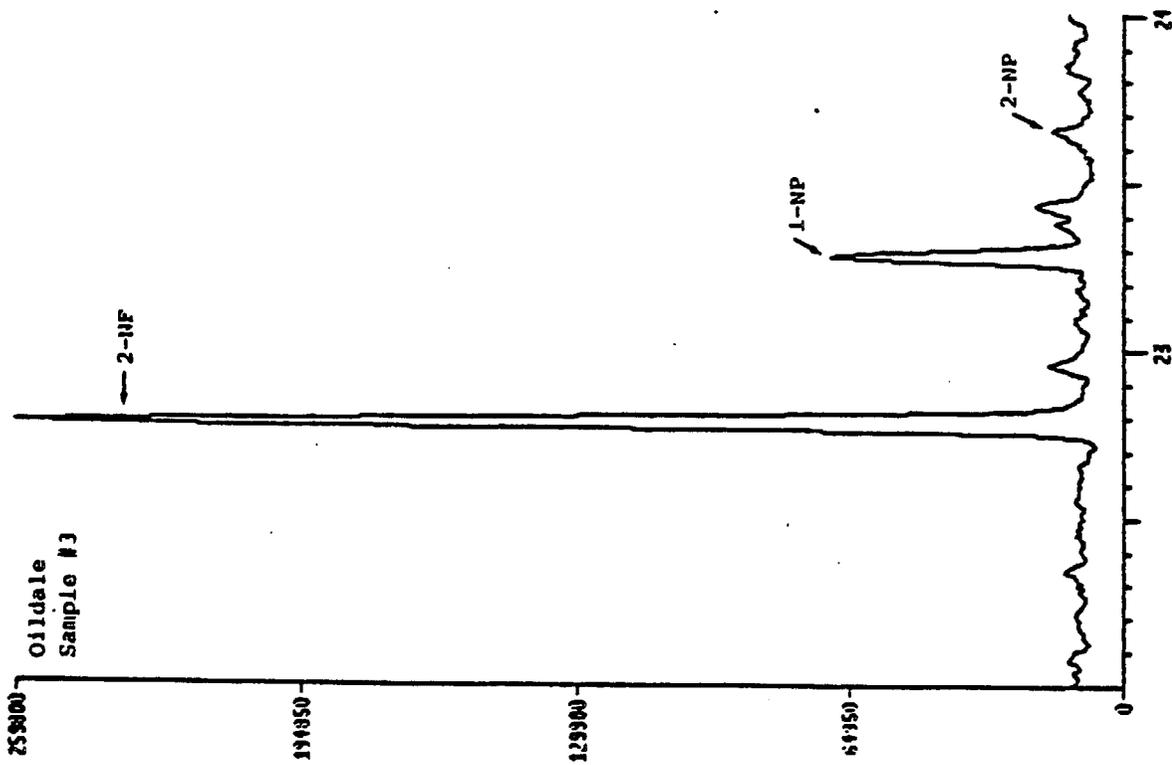


Figure VII-31. GC/MS/MID trace of the molecular ions (m/z 247) of the nitrofluoranthenes (NF) and nitro-pyrenes (NP) in Oildale filter composite, Sample #3.

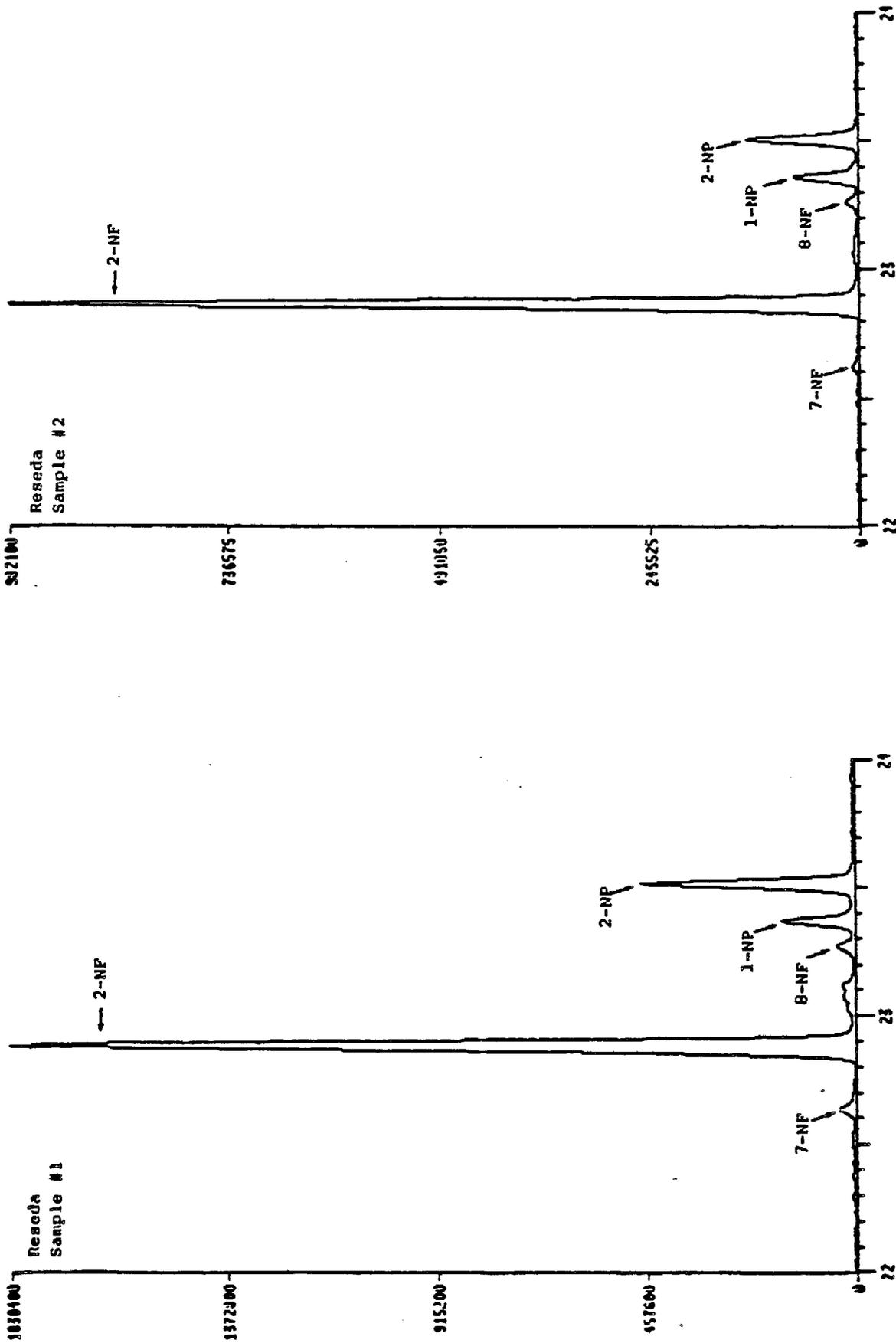


Figure VII-32. GC/MS/MID traces of the molecular ions (m/z 247) of the nitrofluoranthenes (NF) and nitro-pyrenes (NP) in Reseda filter composites, Samples #1 and #2.

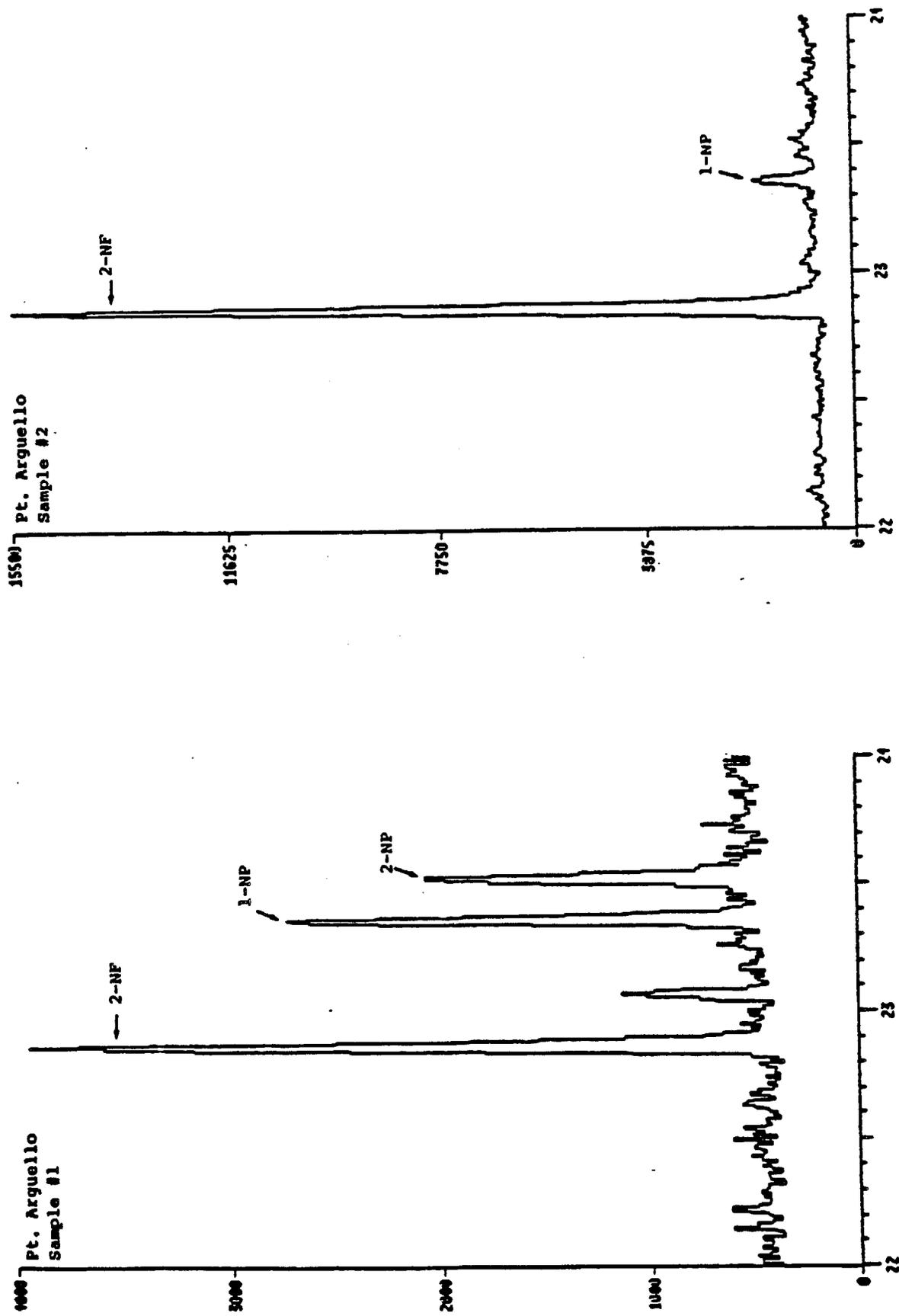


Figure VII-33. GC/MS/MID traces of the molecular ions (m/z 247) of the nitrofluoranthenes (NF) and nitro-pyrenes (NP) in Pt. Arguello filter composites, Samples #1 and #2.

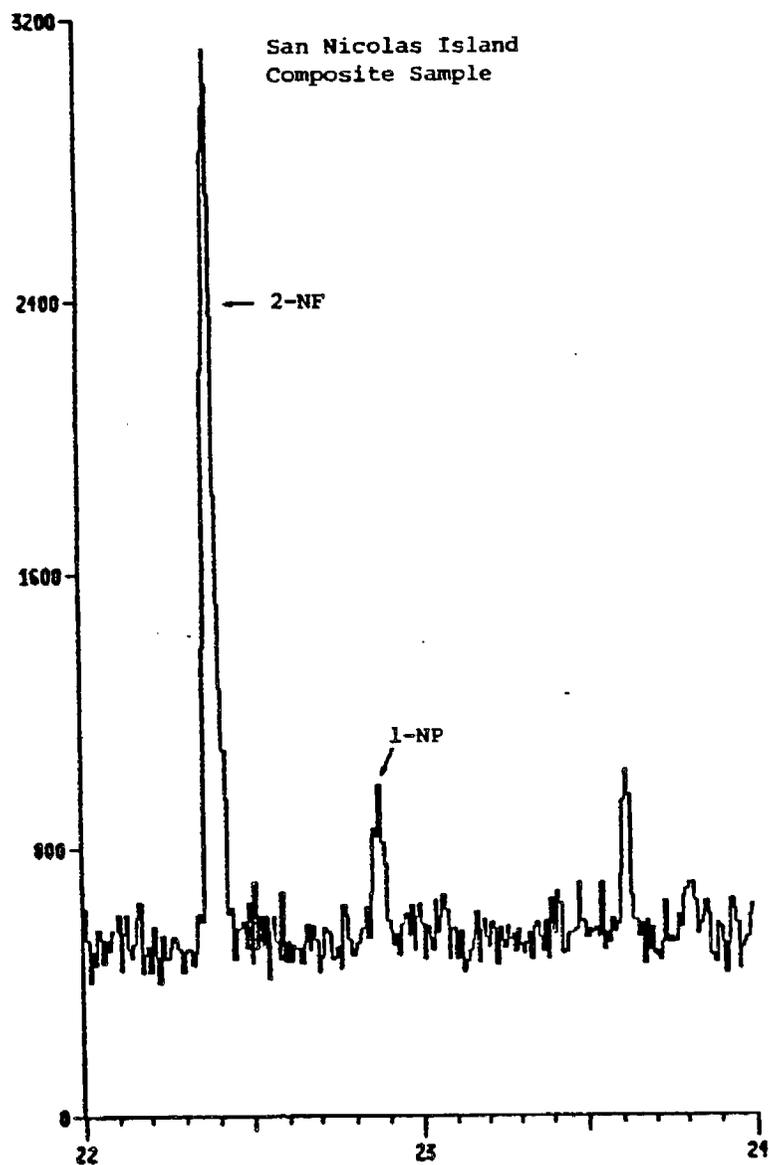


Figure VII-34. GC/MS/MID trace of the molecular ions (m/z 247) of the nitrofluoranthenes (NF) and nitropyrenes (NP) in the San Nicolas Island filter composite.

Table VII-17. Nitronaphthalenes, 9-Nitroanthracene and 7-Nitrobenz[a]anthracene Concentrations Measured for Single or Composited Day/Night Sampling Intervals on TIGF Filters (pg m^{-3}) at the Seven Sampling Sites in California

Location Site and Dates ^a		1-Nitro-naphthalene	2-Nitro-naphthalene ^c	9-Nitro-anthracene	7-Nitro-benz[a]-anthracene (Concord only; see text)
		pg m^{-3} b			
Glendora	Sample #1 Day	63	d	67 ^e	
8/13/86					
Glendora	Sample #2 Night	29	d	95 ^e	
8/13-14/86					
Glendora	Sample #3A Day	77	≤18	180 ^e	
8/15, 16, 17, 18/86					
Glendora	Sample #4A Night	32	≤8.9	250 ^e	
8/15-16, 16-17, 17-18, 18-19/86					
Glendora	Sample #5 Day	13	d	110 ^e	
8/20/86					
Glendora	Sample #6 Night	12	d	250 ^e	
8/20-21/86					
Yuba City	Sample #1 Day	6.0	≤2.9	19 ^e	
10/16, 18, 20/86					
Yuba City	Sample #2 Day	14	≤9.9	f	
10/17, 23/86					
Yuba City	Sample #3 Night	6.8	≤3.0	f	
10/16-17, 18-19, 20-21, 23-24/86					

(continued)

Table VII-17 (continued) - 2

Location Site and Dates ^a		pg m ⁻³ b				7-Nitro- benz[a]- anthracene (Concord only; see text)		
Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	1-Nitro- naphthalene	2-Nitro- naphthalene ^c	9-Nitro- anthracene	
Concord 12/8,9/86; 1/19/87					5.4	≤4.6	110	14
Concord 1/18,21,22/87					8.6	d	270	24 ^h
Concord 12/6-7,7-8,8-9/86					9.1	≤6.1	330	44
Concord 1/17-18,18-19,21-22/87					15	d	660	8
Concord 12/10-11/86; 1/14-15/87					4.0	≤1.8	95	15 ^h
Mammoth Lakes 2/14,16,17,21,22,26,28/87					6.2	8	8	
Mammoth Lakes 2/16-17,17-18,20-21,27-28; 2/28-3/1/87					8	8	8	
Mammoth Lakes 2/14-15,15-16,21-22,22-23,25-26/87					8	8	8	
Oildale 3/30,31/87; 4/1,2,7,8,9,10/87					2.1	d	6.3	

(continued)

Table VII-17 (continued) - 3

Location Site and Dates ^a		1-Nitro-naphthalene	2-Nitro-naphthalene ^c	9-Nitro-anthracene	7-Nitro-benz[a]-anthracene (Concord only; see text)
Oil Dale	Sample #2 Night 3/29-30/87; 4/9-10, 10-11/87	5.2	d	23	
Oil Dale	Sample #3 Night 3/31-4/1/87; 4/1-2, 7-8, 8-9/87	3.7	d	36	
Reseda	Sample #1 Day 5/28, 29, 30, 31/87; 6/1, 2, 14, 15/87	7.2	≤5.4	150	
Reseda	Sample #2 Night 5/27-28, 28-29, 29-30, 30-31, 5/31-6/1; 6/1-2, 2-3, 13-14, 14-15/87	4.1	≤3.2 ^h	28 ^h	
Pt. Arguello	Sample #1 Day 7/4, 5, 6, 7, 8, 9, 10, 11, 12/87	≤1.4	d	≤1.3	
Pt. Arguello	Sample #2 Night 7/4-5, 5-6, 6-7, 7-8, 8-9, 9-10, 10-11, 11-12/87	≤2.4	d	≤2.0	

^aSee Section V for full details of compositing.

^bAverage of replicate GC/MS injections.

^cUpper limit due to interference.

^dNone detected or levels too low to quantify.

^eLower limit; internal standard added after HPLC fractionation.

^fPresent but not quantified due to impurities in internal standard.

^gBackground interference too high to allow for positive identification of nitroarene peak.

^hSingle quantification.

6-Nitrochrysene-d₁₁, two nitrobenz[a]anthracene-d₁₁ isomers, 6-nitrobenzo[a]pyrene-d₁₁ and 3-nitroperylene-d₁₁ were also synthesized after the Glendora samples and Yuba City Sample #1 were extracted and fractionated. These deuterated internal standards were added to the Glendora samples and Yuba City Sample #1 after the second HPLC fractionation (see Section VI-C) and to samples from the remaining sites prior to extraction (the amounts added to Yuba City Samples #2 and #3 were not quantitative since benz[a]anthracene quinone impurities were present in these internal standards). We were unable to analyze for 3-nitroperylene with the GC/MS/MID method used (cool-on-column injection and perhaps a shorter column would be required). Recovery of the 6-nitrobenzo[a]pyrene-d₁₁ standard was reasonable, but only trace amounts of 6-nitrobenzo[a]pyrene were observed in Glendora Sample #6, Concord Sample #1 and Reseda Sample #1.

We observed two nitroarene isomers of M.W. 273 in several samples, which we have identified as 7-nitrobenz[a]anthracene and, tentatively, 9-nitrobenz[a]anthracene (see Figure VII-35). Since the 6-nitrochrysene-d₁₁ internal standard eluted after these two isomers (see Figure VII-35), neither isomer could be 6-nitrochrysene. This finding is significant since 6-nitrochrysene has previously been reported in ambient air samples (Garner et al. 1986, Matsushita and Iida 1986). The estimated ambient concentrations of 7-nitrobenz[a]anthracene for the Concord samples are given in Table VII-17. 7-Nitrobenz[a]anthracene was observed in samples from Glendora, Yuba City and Reseda as well as at Concord, but could not be quantified (full details are given in Table C-18). We feel that without deuterated internal standards to act as a carrier and to correct for losses during the HPLC fractionation procedures, the levels of 7-nitrobenz[a]anthracene would be very much underestimated due to the lability of this nitroarene species.

As we have reported previously, 2-nitrofluoranthene was generally the most abundant particle-associated nitroarene. The present data suggests that 9-nitroanthracene and 7-nitrobenz[a]anthracene may also be relatively high in abundance in ambient samples, perhaps representing direct emissions since these species have also been observed in diesel emissions (MacCrehan et al. 1988).

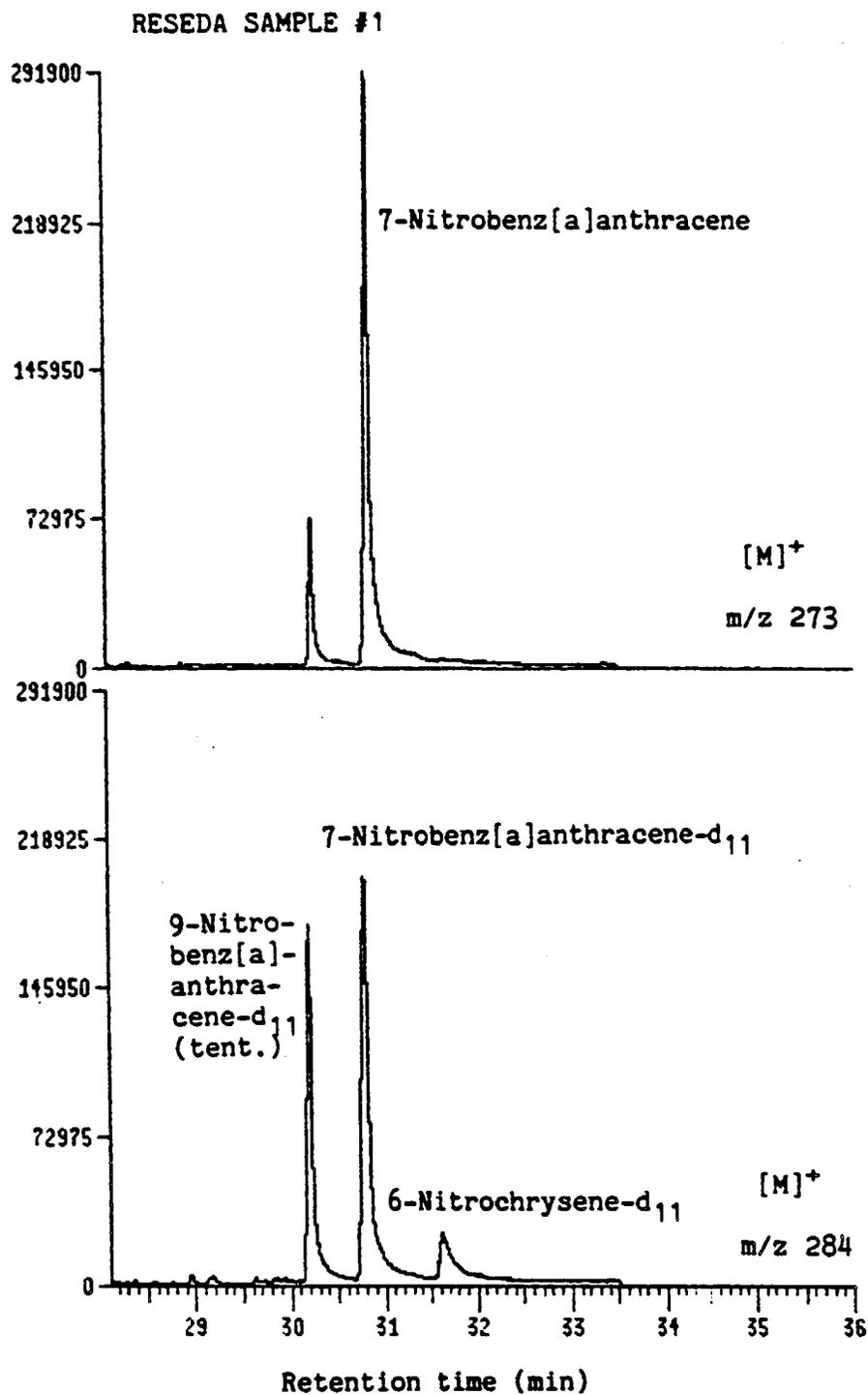


Figure VII-35. GC/MS/MID traces from the analysis of Reseda filter composite Sample #1 for the M.W. 273 nitroarenes, showing the presence of 7-nitrobenz[a]anthracene and, tentatively identified, 9-nitrobenz[a]anthracene. 6-Nitrochrysene was not observed in any of the filter composite samples.

D. Summary of Analyses of Targeted Species

PAH. The results for the PAH targeted for analysis (Table II-5) have been given in the Tables in this section as follows. Naphthalene was quantified from 12-hr "low-flow" Tenax samples, and the ambient concentrations for the seven sites are given in Tables VII-1 through VII-7. Anthracene and phenanthrene were quantified for twenty-four composite PUF plug samples and the results are given in Table VII-9. The majority of the fluoranthene and pyrene was present in the PUF plug samples, with the exception of the Mammoth Lakes and Pt. Arguello samples where large fractions of the fluoranthene and pyrene were present on the filter samples. The results for fluoranthene and pyrene for the twenty-four composite PUF plug samples are given in Table VII-9. The ambient concentrations of fluoranthene, pyrene, benzo[ghi]fluoranthene, cyclopenta[cd]pyrene, benz[a]anthracene, benzo[c]phenanthrene, and chrysene + triphenylene for the twenty-four composite filter samples from the seven sampling sites, for Glendora replicate Samples #3A and #4A, and the San Nicolas Island sample are given in Table VII-11. The ambient concentrations of benzo[b]fluoranthene + benzo[j]fluoranthene + benzo[k]fluoranthene, benzo[a]pyrene and benzo[e]pyrene for these twenty-seven composite filter samples are given in Table VII-13. Lower limits to the ambient concentrations of anthanthrene, benzo[ghi]perylene, indeno[1,2,3-cd]fluoranthene, indeno[1,2,3-cd]pyrene, benzo[b]chrysene, benzo[c]chrysene, dibenz[a,c]anthracene, dibenz[a,h]anthracene, dibenz[a,j]anthracene, picene, and coronene for the twenty-four composite filter samples are given in Table VII-14 (Glendora Samples #3 and #4 and the San Nicolas Island sample were not analyzed for the high M.W. PAH). The following PAH included in Table II-5 could not be quantified: benzo[g]chrysene, dibenzo[a,i]pyrene, dibenz[a,e]aceanthrylene, dibenzo[a,e]pyrene, dibenzo[a,h]pyrene and dibenzo[a,l]pyrene.

Alkyl-PAH. The results for the alkyl-PAH targeted for analysis (Table II-6) are as follows. 1- and 2-Methylnaphthalene were sampled quantitatively only on the Tenax-GC adsorbent cartridges and were quantified from the high-flow Tenax cartridges for eighteen samples at Glendora and for a single day and a single night at each of the other six sites. The results are given in Table VII-8. Isomeric dimethylnaphthalenes were observed on the PUF plug samples, but were not collected quantitatively,

as illustrated in Figure VII-36 which shows the alkyl-naphthalenes observed from simultaneous Tenax and PUF plug samples. The abundances of the alkyl-naphthalenes relative to naphthalene can be seen from the Tenax sample. Clearly the C₂-naphthalenes were less abundant than the methyl-naphthalenes.

The TIC of the PAH-containing HPLC fraction of a Glendora PUF plug sample showed the presence of several methylanthracene or methylphenanthrene isomers, all less abundant than phenanthrene. Due to the number of possible isomers and the lack of standards, no quantifications were attempted. Figure VII-37 gives mass chromatograms for the molecular ion of phenanthrene and anthracene (m/z 178) and their methyl-derivatives (m/z 192) for filter samples from Concord, Mammoth Lakes and Oildale. As discussed in Section VII-C, most of the ambient phenanthrene and anthracene was observed on the PUF plugs rather than on the filters. However, it is apparent from Figure VII-37 that the methylphenanthrenes/methylanthracenes were less abundant than phenanthrene.

In general, the alkyl-PAH of M.W. 242, 266 and 292 were observed to be less abundant than their parent PAH. Figure VII-38 shows the M.W. 228 PAH and their methyl-derivatives. Figure VII-39 shows the M.W. 252 PAH and their methyl-derivatives.

The final alkyl-PAH listed in Table II-6, retene, is a marker for coniferous wood combustion. Its ambient concentration for the twenty-seven composite filter samples is given in Table VII-11.

Hetero-PAH. As discussed in Section VI-C, a method for azaarenes analysis was developed during this program, but the samples have been stored for future analysis due to time and funding constraints. The very limited number of azaarene standards available, with those available being mainly the low M.W. species, contributed to the analytical difficulties.

The only PASH targeted for analysis (Table II-7) for which a standard was available was dibenzothiophene. Fortunately, for this compound a deuterated standard was also available. Due to its volatility, dibenzothiophene was present in the PUF plugs samples rather than in the filters extracts. The ambient dibenzothiophene concentrations for the twenty-four composite PUF plug samples are given in Table VII-9. The PASH are expected to elute with the PAH during the HPLC fractionation. However, no PASH were observed in the TICs from the GC/MS analysis of the PAH fractions in

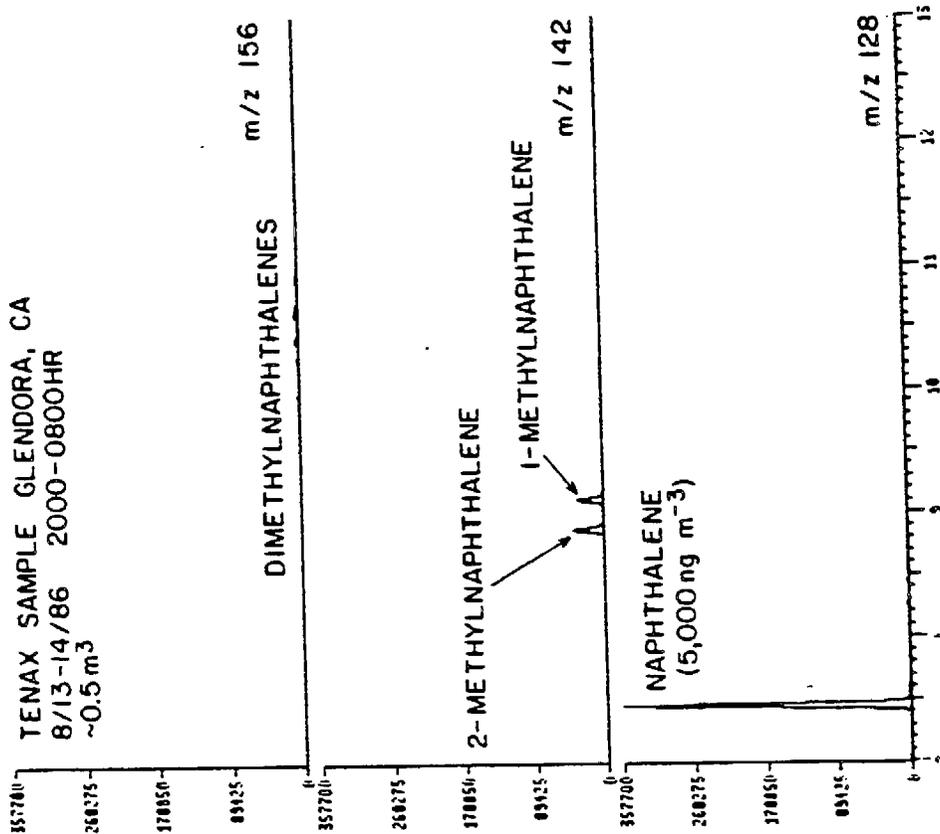
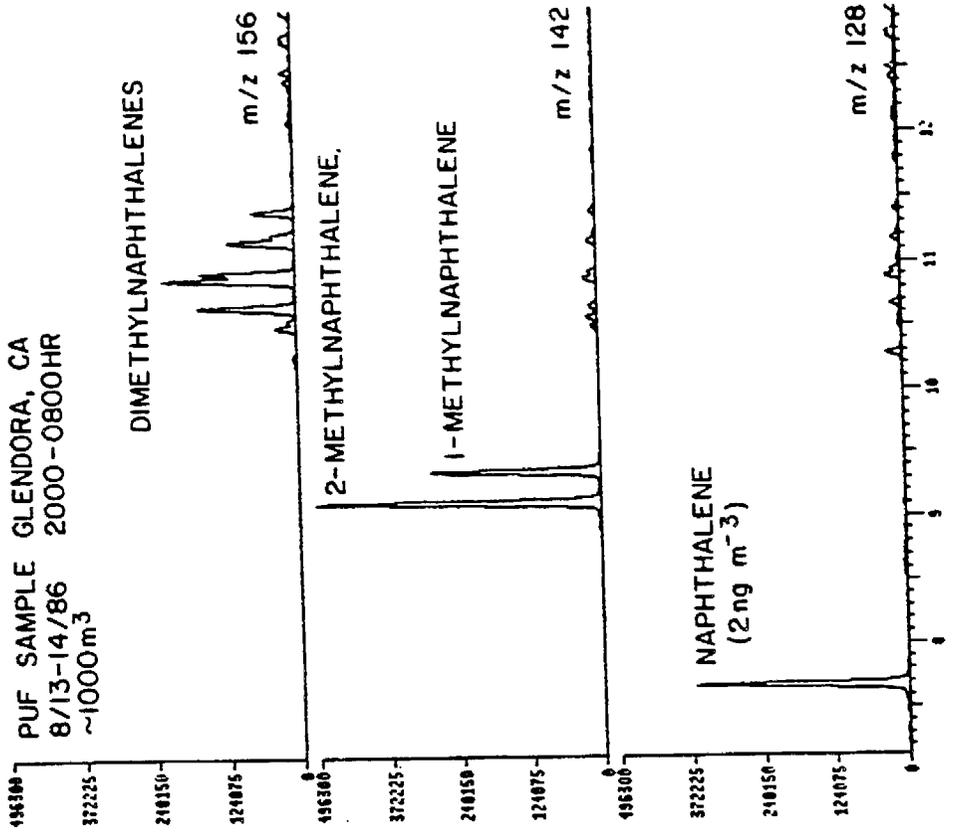


Figure VII-36. GC/MS/MID traces showing the molecular ions of naphthalene (m/z 128), 1- and 2-methyl-naphthalene (m/z 142) and the dimethylnaphthalenes (m/z 156) for analyses of a Tenax-GC (left) and PUF plug (right) sample collected simultaneously in Glendora, CA on 8/13-14/86 from 2000-0800 PDT. The abundances of naphthalene and the alkylnaphthalenes collected on the PUF plug sample are similar and do not reflect the true ambient concentrations. Note the quantitative naphthalene concentration of ~5,000 ng m⁻³ measured by the Tenax sample vs. 2 ng m⁻³ as measured by the PUF sample (from Final Report ARB Contract No. A5-150-32).

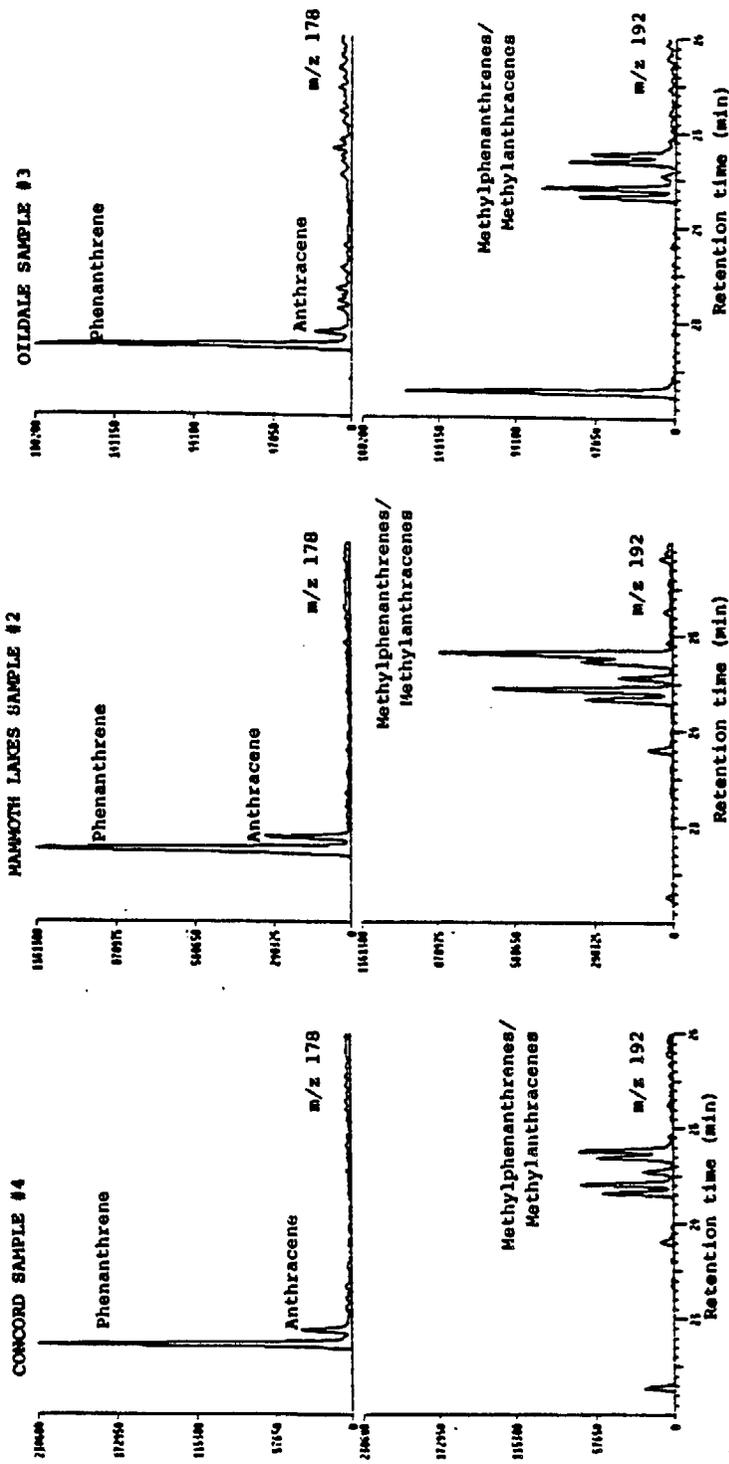


Figure VII-37. Mass chromatograms showing the relative abundances of phenanthrene and anthracene and their methyl-derivatives on filter samples from Concord (Sample #4), Mammoth Lakes (Sample #2) and Oildale (Sample #3). For each sample, the mass chromatograms have been normalized to the height of the phenanthrene peak. It should be noted that most of the ambient phenanthrene and anthracene was observed on the PUF plug samples. The peaks at 22.3 min on the m/z 192 traces are dibenzothiophene-d8, added to the filter samples as an internal standard.

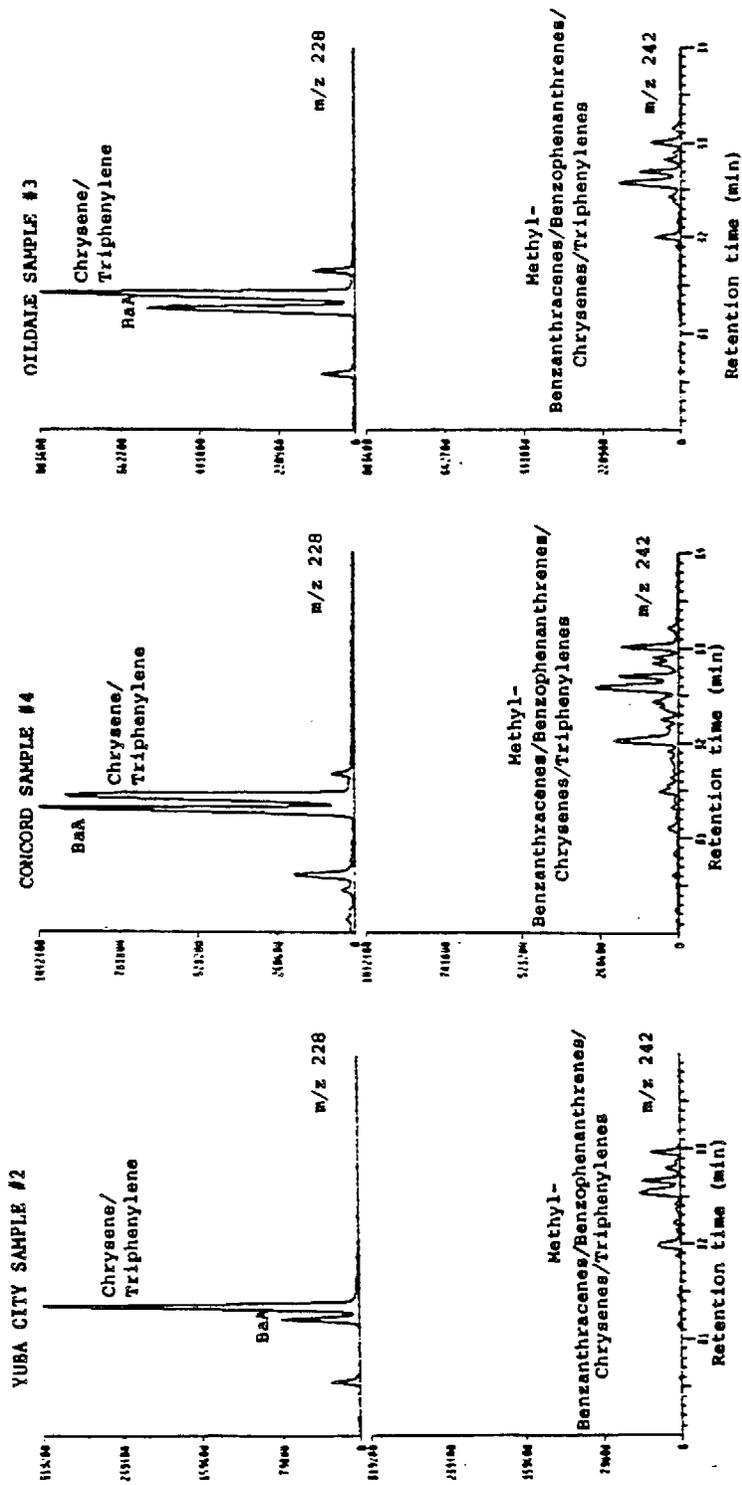


Figure VII-38. MID traces from GC/MS/MID analyses of filter samples from Yuba City (Sample #2), Concord (Sample #4) and Oildale (Sample #3) for the M.W. 228 PAH and their methyl-derivatives. The M.W. 228 PAH (see Figures VII-12 and VII-13) are benzo[a]phenanthrene (30.6 min), benz[a]anthracene (BaA) and co-eluting, chrysene and triphenylene. Note the abundant BaA peak in the Concord sample. Isomer-specific identification of the methyl-derivatives is clearly difficult.

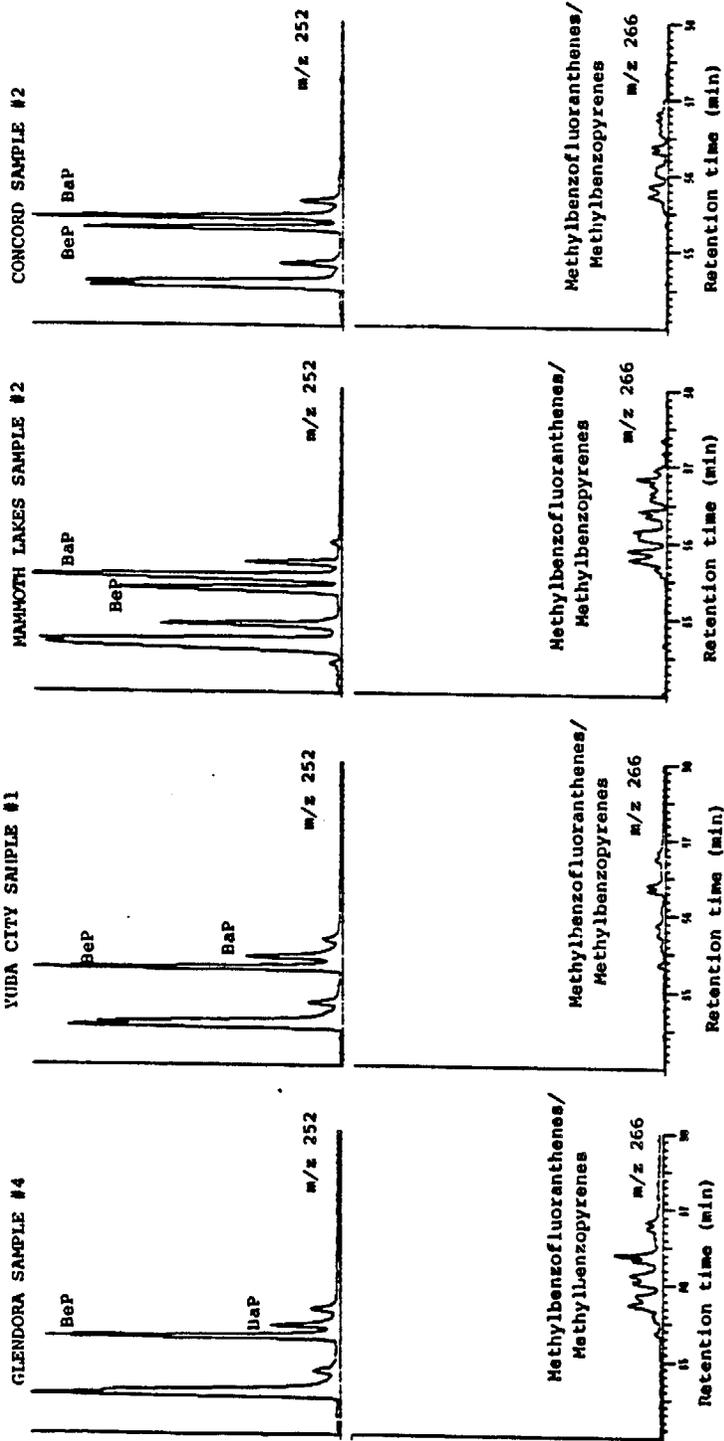


Figure VII-39. MID traces from GC/MS/MID analyses of filter samples from Glendora (Sample #4), Yuba City (Sample #1), Mammoth Lakes (Sample #2) and Concord (Sample #2) for the M.W. 252 PAH and their methyl-derivatives. Benzo[e]pyrene (BeP) and benzo[a]pyrene (BaP) have been labeled on the traces. The earlier eluting peaks are benzo[fluoranthenes and the peak following BaP is perylene (see Figures VII-14 and VII-15). The methyl-derivatives have been labeled as methylbenzofluoranthenes and/or methylbenzopyrenes, but may also include methylperylene.

the full scanning mode, suggesting that, if present, they are less abundant than the PAH in the samples we examined.

Nitroarenes. Of the nitroarenes targeted for analysis (Table II-8), the nitronaphthalenes and nitroarenes of M.W. 199 were expected to be found primarily in the PUF plug samples. The ambient concentrations of 1- and 2-nitronaphthalene and 3-nitrobiphenyl for the twenty-four composite PUF plug samples are given in Table VII-10. 5-Nitroacenaphthene and 4-nitrobiphenyl were not observed in these PUF plug samples (see Figure VII-7).

2-Nitrofluorene was not identified in any of the composite filter samples. However, since we found that our standard of 2-nitrofluorene decomposed with storage (forming 2-nitrofluorenone), it is unlikely that 2-nitrofluorene would be observed without a deuterated internal standard.

The ambient concentrations of 2- and 8-nitrofluoranthene and 1- and 2-nitropyrene, and the observation of trace levels of 3-nitrofluoranthene, are given in Table VII-16 for twenty-five composite filter samples. 7-Nitrofluoranthene was identified in the Reseda samples (see Figure VII-32). 1-Nitrofluoranthene and 4-nitropyrene were not conclusively identified in any of the filter composite samples.

Analysis of the filter samples for 2,7-dinitrofluorene and the dinitropyrenes has not been attempted. At this time we do not have a deuterated internal standard for 2,7-dinitrofluorene. From the analysis of standard solutions of these dinitroarenes, we have determined that cool-on-column injection will be required for their GC/MS/MID analyses. Since the HPLC fraction in which the dinitropyrenes (and also likely 2,7-dinitrofluorene) elute contains a great deal of polar material which will further complicate the analyses, we have not pursued analysis of the dinitroarenes listed in Table II-8 at this time. Since we expect the dinitroarenes in ambient air to be the result of direct emissions, rather than their atmospheric formation, we suggest that the dinitropyrenes [which in diesel emissions are much less abundant than 1-nitropyrene (Scheutzle, 1983)] would be present at levels much below those of 2-nitrofluoranthene in the ambient samples we have reported on here.

Although not included in Table II-8, we have quantified 9-nitroanthracene in the filter composite samples. The ambient concentrations of 9-nitroanthracene and 1- and 2-nitronaphthalene (the majority of the

nitronaphthalenes were observed on the PUF plugs [Table VII-10]) are given in Table VII-17.

7-Nitrobenz[a]anthracene and a second, less abundant, nitrobenz[a]-anthracene isomer were observed in several filter composite samples. Their concentrations of 7-nitrobenz[a]anthracene in the Concord samples have been given in Table VII-17. 6-Nitrochrysene was not observed in any of the samples examined. Only traces of 6-nitrobenzo[a]pyrene were observed in the filter samples and 3-nitroperylene could not be quantified at this time.

Sections X and XI discuss the implications of the large data bases which have been presented in this section (PAH and nitroarene concentrations) and Section IV (mutagenicity) and treat the relationships between the chemical data and mutagenicity.

VIII. MUTAGENICITY AND PAH DATA FROM TORRANCE

During a previous SAPRC ARB-funded study (Contract No. A4-081-32), we employed experimental protocols similar to those utilized in this study to sample ambient air at a location in Torrance, CA, for mutagenicity testing and chemical analysis. The results of this previous study are hence of interest to the present study. Although the data base for this Torrance site is much more limited than the data bases for the seven sites studied here, it does provide information concerning PAH and PAH-derivative concentrations and ambient POM mutagenicities for a site which appeared to be impacted by vehicle emissions and industrial emissions.

Sampling was carried out from the roof of a two-story building at the north side of El Camino Community College, Torrance, a site approximately 20 km southwest of downtown Los Angeles and 8 km east of the coast. Ambient air samples were collected for day/night periods on January 19/20, January 27/28 and February 24/25, 1986. These sampling periods were characterized by clear sky conditions and generally low inversion heights. The January 19/20 sampling period had low pollutant levels, with NO_x concentrations generally below 100 ppb. However, for the January 27/28 and February 24/25 sampling periods, the NO_x (mainly NO) levels exceeded 500 ppb during the early morning peak traffic hours (0700-0900 hr) and the maximum NO_2 concentrations, attained at 1000 hr on both mornings, were approximately 250 ppb. Ozone concentrations were low, and NO_3 radicals (and hence N_2O_5) were not expected to be present.

Temperatures ranged from 60°F during the nights to 95°F during the daytime. Complete details of this study are given in our final report to Contract No. A4-081-32 ("The Role of Nitrogenous Pollutants in the Formation of Atmospheric Mutagens and Acid Deposition"), and only those data relevant to this present study are given in this section. The extraction, fractionation and analysis (both chemical and mutagenic) procedures were similar to those used here, with the exception that the PUF plugs and the filters were extracted with CH_2Cl_2 prior to fractionation and/or analysis, and that mutagenicity testing was not carried out in the presence of S9.

The Tenax, PUF plug and filter samples were analyzed for PAH and nitroarene concentrations only for two 12-hr sampling periods. These data

for February 24-25 (1800-0600 PST) and February 25 (0600-1800 PST) are given in Tables VIII-1 and VIII-2. Filter samples from several 12-hr time periods were analyzed for nitrofluoranthenes and nitropyrenes. Table VIII-3 gives the observed concentrations of the nitroarenes of molecular weight 247. The mutagenicity data, in terms of revertants m^{-3} , are given in Table VIII-4 for the January 27/28 and February 24/25 time periods corresponding to those for which chemical analyses were carried out.

When these PAH concentrations and mutagenicity levels are compared with those measured in this study at the various sites throughout California, it is evident that this Torrance site ranked high on the overall list with respect to both the ambient POM mutagenicity and the PAH concentrations, especially during the January 27/28 and February 24/25 sampling periods. Indeed, these data indicate that this site was somewhat similar to the Concord site in that PAH emissions were high, with a considerable amount of atmospheric transformation products (such as 2-nitrofluoranthene and 2-nitropyrene) being present, with concurrent high ambient mutagen densities.

Table VIII-1. Ambient Concentrations (ng m^{-3}) of PAH and Nitroarenes. Nighttime Sample Collected at El Camino Community College, Torrance, CA, February 24 - 25, 1986, 1800 - 0600 PST

Compound	M.W.	ng m^{-3}					Filter	$\Sigma(\text{Filter} + \text{PUF's})$	Tenax
		PUF#1	PUF#2	PUF#3	Filter	$\Sigma(\text{Filter} + \text{PUF's})$			
<u>PAH</u>									
Naphthalene	128	29	24	22	0.27	75	2,800		
2-Methylnaphthalene	142	a	a	a			1,100		
1-Methylnaphthalene	142	a	a	a			1,200		
Biphenyl	154	a	a	a			62		
Phenanthrene	178	70	9.4	1.0	0.28	81	90		
Anthracene	178	9.5	1.5	0.28	0.03	11	7.2		
Fluoranthene	202	9.1	0.06	b	0.53	9.7			
Pyrene	202	8.8	2.7 ^c	b	0.67	12			
Benzo[e]pyrene	252	b			2.1	2.1			
Benzo[a]pyrene	252	b			1.6	1.6			
Perylene	252	b			0.47	0.5			
<u>Nitroarenes</u>									
1-Nitronaphthalene	173	1.6	0.53	0.12	0.01	2.3			
2-Nitronaphthalene	173	0.90	0.19	0.03	0.002	1.1			
3-Nitrobiphenyl	199	0.38	0.15	0.04	0.01	0.6			
9-Nitroanthracene	223	b			0.11	0.1			
2-Nitrofluoranthene	247	0.04			0.32	0.4			
1-Nitropyrene	247	b			0.03	0.03			
2-Nitropyrene	247	b			0.03 ^d	0.03			

^aAs was the case with naphthalene, each PUF retained a similar small amount of this compound and was therefore not useful for quantification purposes.

^bNone detected.

^cValue suspect; see, for example, fluoranthene in this table, and fluoranthene and pyrene in Table VIII-2.

^dQuantification by reverse phase HPLC.

Table VIII-2. Ambient Concentrations (ng m^{-3}) of PAH and Nitroarenes. Daytime Sample Collected at El Camino Community College, Torrance, CA February 25, 1986, 0600 - 1800 PST

Compound	M.W.	ng m^{-3}							Tenax
		PUF#1	PUF#2	PUF#3	Filter	$\Sigma(\text{Filter} + \text{PUF's})$			
<u>PAH</u>									
Naphthalene	128	4.7	4.5	4.9	0.45	15		3,300	
2-Methylnaphthalene	142	a	a	a				900	
1-Methylnaphthalene	142	a	a	a				1,100	
Biphenyl	154	a	a	a				60	
Phenanthrene	178	33	32	13	0.33	78		78	
Anthracene	178	2.3	2.7	1.1	0.03	6.1			
Fluoranthene	202	7.1	0.44	b	0.47	8.0			
Pyrene	202	7.0	0.36	b	0.60	8.0			
Benzo[e]pyrene	252	b			2.1	2.1			
Benzo[a]pyrene	252	b			0.59	0.6			
Perylene	252	b			0.18	0.2			
<u>Nitroarenes</u>									
1-Nitronaphthalene	173	1.3	1.0	0.67	0.05	3.0 ^c			
2-Nitronaphthalene	173	1.4	1.1	0.38	0.006	2.9			
3-Nitrobiphenyl	199	5.7	0.29	0.01	0.03	6.0			
9-Nitroanthracene	223	b			0.05	0.05			
2-Nitrofluoranthene	247	0.009			0.28	0.3			
1-Nitropyrene	247	b			0.04	0.04			
2-Nitropyrene	247	b			0.04	0.04			

^aAs was the case with naphthalene, each PUF retained a similar small amount of this compound and was therefore not useful for quantification purposes.

^bNone detected.

^cLower limit, due to the observed breakthrough through the three PUF's used.

Table VIII-3. Concentrations of Nitrofluoranthenes (NF) and Nitropyrenes (NP) in Ambient Particulate Samples Collected at Torrance

Date of Collection	Collection Time (PST)	Concentration, $\mu\text{g m}^{-3}$ ($\mu\text{g g}^{-1}$)					$\frac{2\text{-NFA}}{2\text{-NP}}$
		2-NF	3-NF	8-NF	1-NP	2-NP	
1/19-20/86 ^b	1700-0500	40 (0.7)	c	c	3 (0.05)	1 (0.02)	40
1/20/86 ^b	0500-1700	60 (0.8)	c	c	10 (0.1)	1 (0.02)	60
1/27-28/86	1700-0500	750 (6)	70 (0.5)	50 (0.4)	50 (0.4)	60 (0.4)	12
1/28/86	0500-1700	410 (3)	3	8 (0.07)	60 (0.5)	50 (0.4)	8
2/24-25/86	1800-0600	320 (4)	c	c	30 (0.4)	30 (0.4)	11
2/25/86	0600-1800	280 (2)	c	c	40 (0.2)	40 (0.2)	7

^aBased on $\mu\text{g m}^{-3}$ values. The ratios based on $\mu\text{g g}^{-1}$ values may differ slightly, due to rounding.
^bAnalyzed on a 30-m DB-5 column, therefore with a poorer limit of detection for 3- and 8-NF than for the samples analyzed on a 60-m DB-5 column.

^cNot quantified; either none of the compound was detected or the levels present were too low to be quantified.

Table VII-4. Direct Mutagenicity of Ambient POM at Torrance

Collection Date	Collection Time (PST)	Mutagen Density ^a rev m ⁻³
1/27-28/86	1700-0500	120
1/28/86	0500-1700	120
2/24-25/86	1800-0600	35 ^b
2/25/86	0600-1800	73

^aTested on TA98, -S9; CH₂Cl₂, extracts of POM collected on TIGF filters.

^bAverage of two six-hour samples.

IX. ATMOSPHERIC REACTIONS OF PAH AND FORMATION OF NITROARENES

As a result of two decades of laboratory, environmental chamber and ambient atmospheric measurements, it is now recognized that all chemical compounds emitted into the troposphere are removed from the atmosphere by a number of physical and chemical processes. PAH emitted into the atmosphere exhibit a range of volatilities (Table IX-1) and are partitioned between the gas- and particulate-phases. The available ambient air data show the 2-4 ring PAH exist, at least partially, in the gas phase (see Coutant et al. 1988 and Section VII). Thus, the atmospheric loss-processes for both of these phases must be evaluated separately.

The physical removal processes can be defined in a simplistic manner as consisting of dry and wet deposition of gases and particles. Removal of gases and particles at ground surfaces (including snow and other moist surfaces) is referred to as dry deposition, while removal of these species by raindrops is referred to as wet deposition. Our current understanding of these processes, which are dynamic in nature, must still be judged to be semi-quantitative.

For PAH present in the gas phase the chemical removal processes which are expected to be important are:

- Photolysis during daylight hours.
- Reaction with hydroxyl (OH) radicals during daylight hours.
- Reaction with ozone (O_3) during, typically, both daytime and nighttime.
- Reaction with the gaseous nitrate (NO_3) radical during nighttime hours.
- Reaction with dinitrogen pentoxide (N_2O_5) during nighttime hours.

For the PAH present in the adsorbed phase, the same chemical removal processes are possible. However, it is likely that those involving reactions with radicals (OH and NO_3) will either not occur or be insignificant, since the water layers typically present on particles will not allow radicals (or N_2O_5) to penetrate into particles. Additional reaction processes involving species such as NO_2 , HNO_3 and H_2O_2 could, however, be significant.

As presently understood, dry deposition is of essentially negligible importance as an atmospheric removal process for gas-phase PAH. Wet

Table IX-1. Vapor Pressures at 298 K for a Series of PAH^a

PAH	Vapor Pressure at 298 K (torr)
Naphthalene	8.0×10^{-2}
Acenaphthylene	6.7×10^{-3}
Acenaphthene	2.2×10^{-3}
Fluorene	6.0×10^{-4}
Phenanthrene	1.2×10^{-4}
Anthracene	6.0×10^{-6}
Fluoranthrene	9.2×10^{-6}
Pyrene	4.5×10^{-6}
Benzo[a]anthracene	2.1×10^{-7}
Benzo[a]pyrene	5.6×10^{-9b}
Chrysene	6.4×10^{-9b}

^aFrom Sonnefeld et al. (1983), except as indicated.

^bFrom Yamasaki et al. (1984).

deposition of gas-phase PAH appears to be relatively slow, based upon the literature washout ratios of approximately 100-300 for naphthalene and 2000-4000 for pyrene (Ligocki et al. 1985) and the fact that chemicals which are very rapidly wet deposited have washout ratios of 10^5 to 10^6 . In contrast, the particle-associated PAH will readily undergo wet deposition, since particles are rapidly washed out with washout ratios of 10^5 to 10^6 . However, wet deposition is episodic in nature, especially in southern California.

Adsorbed-Phase Reactions of PAH. Since many PAH and their analogues and derivatives are partitioned primarily into the adsorbed phase under atmospheric conditions, a number of experimental studies have been carried out to delineate the reaction processes occurring for these adsorbed species. However, most of these studies have been carried out on non-atmospherically realistic adsorbents, such as glass fiber and Teflon-impregnated glass fiber and silica surfaces. The data obtained from these

and from more realistic surfaces such as carbon black and fly-ash show that any reactions occurring, including photolysis, are strongly dependent on the nature of the adsorbent species (see, for example, Pitts 1983, Behymer and Hites 1985).

To date, photolysis and reaction with O_3 , NO_2 and/or HNO_3 and N_2O_5 have all been shown to lead to loss of PAH on several substrates (see, for example, Pitts 1979, 1983; Pitts et al. 1978, 1980, 1985b,c, 1986). Certain of these reactions, for example, those with NO_2/HNO_3 and N_2O_5 , appear to be relatively slow under atmospheric conditions (Pitts et al. 1985b). However, because of the substrate dependence of these adsorbed-phase reactions, no firm conclusions can be drawn concerning the importance of these reactions under atmospheric conditions, although it appears that photolysis and reaction with O_3 may be important for certain PAH and their derivatives (Behymer and Hites 1978, Pitts et al. 1986).

We have recently conducted, under ARB funding, a study designed to evaluate the potential for "artifact" nitroarene formation during collection of ambient POM using standard Hi-vol samplers (Arey et al. 1988). In this study, perdeuterated fluoranthene, pyrene, benzo[a]pyrene and perylene were coated onto POM precollected on TIGF filters, which were then used under normal high volume sampling conditions for 12-hour daytime and nighttime collection periods. The amounts of deuterated nitroarenes formed under these conditions were very low (<0.1% of the parent deuterated PAH) and for the nitrofluoranthenes and nitropyrenes were minor compared to the amounts of nitroarenes observed in the POM (for comparable loadings of deuterated and non-deuterated PAH on the filters). Hence, nitroarene formation during collection of ambient POM can be discounted (Arey et al. 1988).

The more recent data from our own work, as well as literature studies (Schuetzle and Frazier 1986, Coutant et al. 1988), suggest that the particle-associated PAH are to a large extent protected against reaction during transport from source-to-receptor. This probably occurs because a substantial fraction of these less-volatile (>5 ring) PAH are present inside the particles, and thus cannot react with atmospheric gas-phase species. Hence, only those PAH which are either present on the outside of the particles or can migrate within the particles undergo reaction.

Gas-Phase Reactions of PAH. The chemical atmospheric removal processes of PAH have received experimental attention only during the past few years. Rate constants at room temperature for the gas-phase reactions of the lower molecular weight PAH with OH and NO₃ radicals, O₃ and N₂O₅ have been determined, and the available data are listed in Table IX-2. When these kinetic data are combined with the measured or calculated atmospheric concentrations of OH and NO₃ radicals and O₃ and N₂O₅, the atmospheric gas-phase lifetimes of the PAH due to reaction with each of these reactive species can be estimated and these are given in Table IX-3. The following tropospheric concentrations were used for these calculations: OH radicals, 1.5×10^6 molecule cm⁻³ during daylight hours (Prinn et al. 1987); O₃, 7×10^{11} molecule cm⁻³, representative of background levels throughout a 24-hr period (Singh et al. 1978); NO₃ radicals, 2.4×10^8 molecule cm⁻³ during nighttime hours (Platt et al. 1984, Atkinson et al. 1986); and N₂O₅, 2×10^{10} molecule cm⁻³ during nighttime hours (Atkinson et al. 1986). Clearly, as far as a tropospheric loss process for gas-phase PAH not containing cyclopenta-fused rings, the daytime reaction with the OH radical is totally dominant, leading to atmospheric lifetimes of one day or less. Indeed, for peak noontime OH concentrations of $(3-4) \times 10^6$ molecule cm⁻³, the lifetimes of these PAH can be as short as 1 hr or less. The O₃ reactions are generally completely negligible except for acenaphthylene and (probably) acephenanthrylene, while the reactions with N₂O₅ are of minor importance as a PAH loss process. For the PAH containing cyclopenta-fused rings, such as acenaphthene and acenaphthylene and (presumably) acephenanthrylene, the NO₃ radical reactions can be important gas-phase loss processes during nighttime hours.

Relatively few product data are available concerning these gas-phase PAH reactions. However, it has recently been shown that, in the presence of NO_x, the OH radical reactions with naphthalene, biphenyl, fluoranthene, pyrene and acephenanthrylene lead to the formation of nitroarenes (Arey et al. 1986, Atkinson et al. 1987a,b, Zielinska et al. 1988b). Specifically, naphthalene forms 1- and 2-nitronaphthalene, biphenyl forms 3-nitrobiphenyl, fluoranthene forms 2-nitrofluoranthene together with lesser amounts of 7- and 8-nitrofluoranthene, and pyrene forms 2-nitropyrene together with lesser amounts of 4-nitropyrene. These products, and their measured or estimated yields, are given in Table IX-4.

Table IX-2. Rate Constants for the Gas-Phase Reactions of PAH with OH and NO₃ Radicals, N₂O₅ and O₃ at Room Temperature

PAH	Rate Constant (cm ³ molecule ⁻¹ s ⁻¹) for Reaction with			
	OH	NO ₃	N ₂ O ₅	O ₃
Naphthalene	2.2 x 10 ⁻¹¹ ^a	b	1.4 x 10 ⁻¹⁷ ^c	<2 x 10 ⁻¹⁹ ^d
Biphenyl	7 x 10 ⁻¹² ^a	b	<2 x 10 ⁻¹⁹ ^c	<2 x 10 ⁻¹⁹ ^d
1-Methylnaphthalene	5.3 x 10 ⁻¹¹ ^e	b	3.3 x 10 ⁻¹⁷ ^e	<1.3 x 10 ⁻¹⁹ ^e
2-Methylnaphthalene	5.2 x 10 ⁻¹¹ ^f	b	4.2 x 10 ⁻¹⁷ ^e	<4 x 10 ⁻¹⁹ ^f
2,3-Dimethylnaphthalene	7.7 x 10 ⁻¹¹ ^f	b	5.7 x 10 ⁻¹⁷ ^e	<4 x 10 ⁻¹⁹ ^f
Acenaphthene	1.0 x 10 ⁻¹⁰ ^g	4.6 x 10 ⁻¹³ ^g	5.5 x 10 ⁻¹⁷ ^g	<5 x 10 ⁻¹⁹ ^g
Acenaphthylene	1.1 x 10 ⁻¹⁰ ^g	5.4 x 10 ⁻¹² ^g		5.5 x 10 ⁻¹⁶ ^g
Phenanthrene	3.4 x 10 ⁻¹¹ ^h			
Anthracene	1.3 x 10 ⁻¹⁰ ^h			

^aAtkinson (1986).

^bNo reaction with NO₃ radicals observed.

^cAtkinson et al. (1987b).

^dAtkinson et al. (1984).

^eAtkinson and Aschmann (1987).

^fAtkinson and Aschmann (1986).

^gAtkinson and Aschmann (1988).

^hBiermann et al. (1985).

Table IX-3. Calculated Atmospheric Lifetimes of the PAH Due to Gas-Phase Reaction with OH and NO₃ Radicals, N₂O₅ and O₃

PAH	Lifetime Due to Reaction with			
	OH ^a	NO ₃ ^b	N ₂ O ₅ ^c	O ₃ ^d
Naphthalene	8.4 hr	e	83 days	>80 days
Biphenyl	2.2 days	e	>1.6 yr	>80 days
1-Methylnaphthalene	3.5 hr	e	35 days	>125 days
2-Methylnaphthalene	3.6 hr	e	28 days	>40 days
2,3-Dimethylnaphthalene	2.4 hr	e	20 days	>40 days
Acenaphthene	1.9 hr	~3 hr	25 days	>30 days
Acenaphthylene	1.7 hr	13 min	f	~48 min
Phenanthrene	5.4 hr			
Anthracene	1.4 hr			

^aFor 12-hr daytime OH radical concentration of 1.5×10^6 molecule cm⁻³ (Prinn et al. 1987).

^bFor 12-hr nighttime NO₃ radical concentration of 2.4×10^8 molecule cm⁻³ (Atkinson et al. 1986).

^cFor 12-hr nighttime N₂O₅ concentration of 2×10^{10} molecule cm⁻³ (Atkinson et al. 1986).

^dFor 24-hr average O₃ concentration of 7×10^{11} molecule cm⁻³ (Singh et al. 1978).

^eNo reaction observed.

^fNo N₂O₅ reaction observed.

Table IX-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 N₂O₅, Together with their Yields

PAH	Reaction with	
	OH	N ₂ O ₅
Naphthalene	1-Nitronaphthalene (0.3%) ^a	1-Nitronaphthalene (17%) ^a
	2-Nitronaphthalene (0.3%) ^a	2-Nitronaphthalene (7%) ^a
Pyrene	2-Nitropyrene (~0.5%) ^b	4-Nitropyrene ^c
	4-Nitropyrene (~0.05%) ^d	
Fluoranthene	2-Nitrofluoranthene (~5%) ^b	2-Nitrofluoranthene ^e
	7-Nitrofluoranthene (~0.2%) ^b	
	8-Nitrofluoranthene (~0.2%) ^b	
Acephen- anthrylene	Two nitroarene isomers (~0.1%) ^f	None observed ^f
Biphenyl	3-Nitrobiphenyl (5%) ^a	No reaction observed ^a

^aAtkinson et al. (1987b).

^bArey et al. (1986).

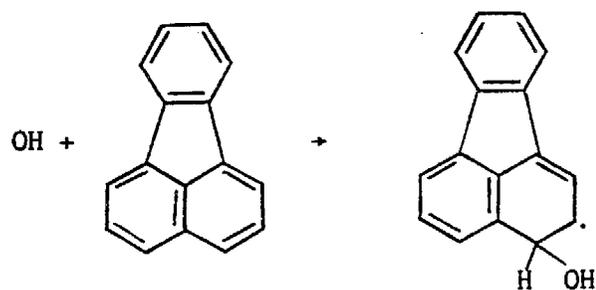
^cYield ~100 times lower than that for 2-nitrofluoranthene from N₂O₅ reaction (this laboratory, unpublished data).

^dEstimated yield (this laboratory, unpublished data).

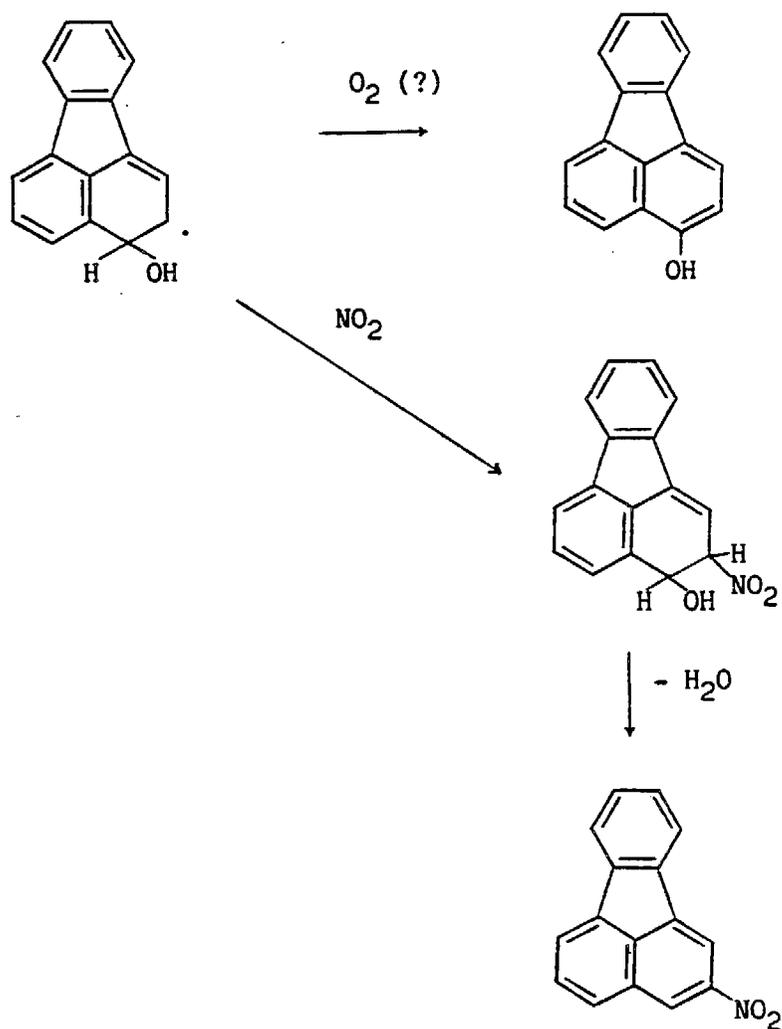
^eSweetman et al. (1986).

^fZielinska et al. (1988b).

The postulated reaction pathway involves initial OH radical addition at the most reactive position; for example, for fluoranthene



followed by reactions to form the hydroxy-PAH or nitroarenes



This reaction scheme accounts for the nitroarenes observed from these reactions, and is supported by the observation of 1- and 2-hydroxynaphthalene from naphthalene and 2-hydroxybiphenyl (together with much smaller amounts of 3- and 4-hydroxybiphenyl) from biphenyl (Atkinson et al. 1987b).

The gas-phase reaction of N_2O_5 with naphthalene yields ~25% of the 1- and 2-nitronaphthalenes (Pitts et al. 1985b, Atkinson et al. 1987b) and the available experimental data concerning the nitroarene yields from the N_2O_5 reactions are given in Table IX-4. Thus, the two nitronaphthalene isomers and 2-nitrofluoranthene can be formed from both OH radical and N_2O_5 reaction, while 3-nitrobiphenyl and 2-nitropyrene are only formed in the gas phase from the OH radical reactions. It is of interest to evaluate the relative importance of these formation routes involving the gas-phase reactions of PAH with N_2O_5 and with OH radicals, in the presence of NO_x , for the formation of nitroarenes. Using naphthalene as an example, for an ambient nighttime N_2O_5 concentration of 2×10^{10} molecule cm^{-3} the 2-nitronaphthalene formation rate is $\sim 2 \times 10^{-8}$ [naphthalene] s^{-1} . This corresponds to a conversion rate of gas-phase naphthalene to 2-nitronaphthalene of $\sim 0.01\%$ hr^{-1} . With the 2-nitronaphthalene yield from the gas-phase OH radical reaction with naphthalene of $\sim 0.3\%$ and an OH radical rate constant of 2.2×10^{-11} cm^3 molecule $^{-1}$ s^{-1} , the 2-nitronaphthalene formation rate for a daytime OH radical concentration of 1.5×10^6 molecule cm^{-3} is $\sim 1 \times 10^{-7}$ [naphthalene] s^{-1} , corresponding to $\sim 0.04\%$ hr^{-1} conversion of gas-phase naphthalene to 2-nitronaphthalene. Thus, with the kinetic and product yield data presently available, these two 2-nitronaphthalene formation pathways appear to be of similar magnitude, and hence both the daytime OH radical and nighttime N_2O_5 reactions must be considered as formation routes to 2-nitronaphthalene and other nitroarenes.

These expectations are consistent with our ambient atmospheric data (Sections VII and VIII and Final Report to ARB Contract No. A4-081-32), which show that 2-nitrofluoranthene is generally the major, and 2-nitropyrene one of the major, nitroarene component of ambient POM. Figure IX-1 shows a comparison of these nitroarenes in wintertime Torrance samples (where N_2O_5 was absent or negligible) with summertime Claremont samples, where N_2O_5 was expected to be present (Biermann et al. 1986).

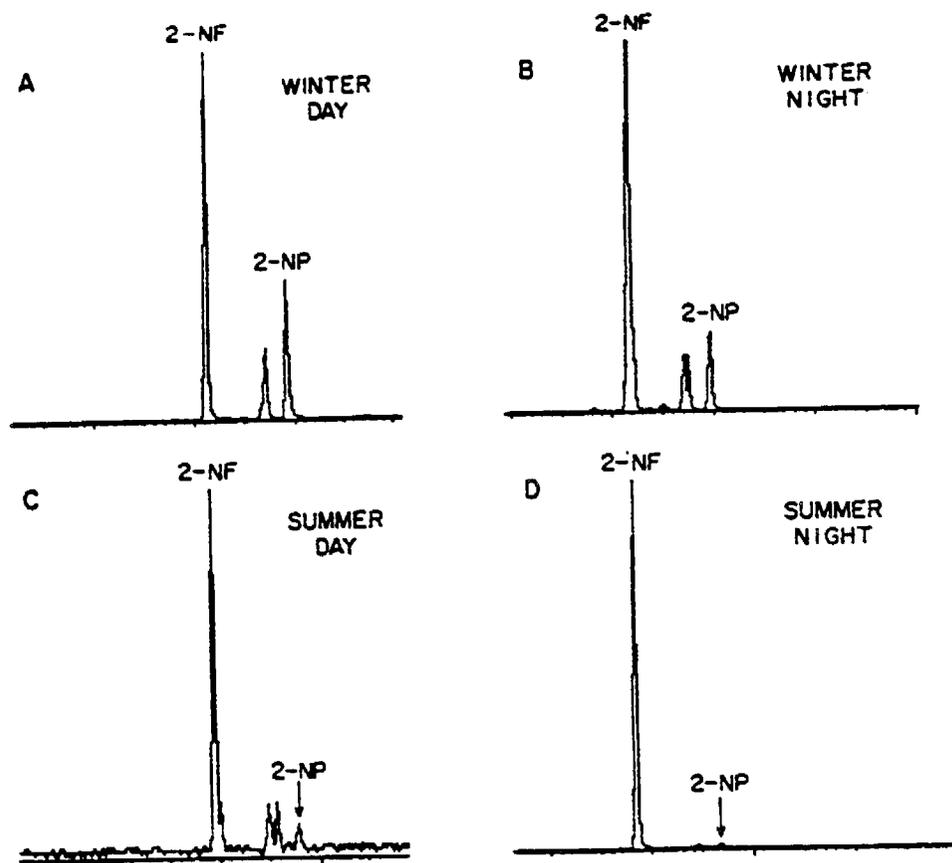


Figure IX-1. GC-MS MID traces of the molecular ions of the nitrofluoranthene (NF) and nitropyrene (NP) isomers present in ambient POM. The sample extraction and clean-up procedures have been described previously (Arey et al. 1987). The ambient particulate samples were collected as follows:
 (A) at Torrance, CA on January 28, 1986 from 0500-1700 hr.
 (B) at Torrance, CA on January 27-28, 1986 from 1700-0500 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.

The nitroarenes consistently present in these ambient POM samples were 2-nitrofluoranthene, 1-nitropyrene, and 2-nitropyrene, in agreement with other recent analyses of ambient POM samples collected in the U.S. and Europe (Nielsen et al. 1984, Pitts et al. 1985a, Liberti and Ciccioli 1986, Nielsen and Ramdahl 1986, Ramdahl et al. 1986, Sweetman et al. 1986).

While 1-nitropyrene is emitted from combustion sources such as diesel (Paputa-Peck et al. 1983, Robbat et al. 1986) and gasoline (Gibson 1982, Nishioka et al. 1982) fueled engines and coal-fired commercial power

plants (Harris et al. 1984), 2-nitrofluoranthene and 2-nitropyrene have not been reported to be present in these combustion emissions. A single report of the presence of 2-nitrofluoranthene and 2-nitropyrene in an industrial emission (from a plant manufacturing carbon electrodes) has recently appeared (Liberti and Ciccioli 1986). This particular industrial emission source seems unlikely to be a major contributor to ambient 2-nitrofluoranthene and 2-nitropyrene concentrations, except perhaps on a very local scale. Although more detailed studies of the nitroarene isomers emitted from various industrial sources are needed, the observations of 2-nitrofluoranthene and 2-nitropyrene in ambient POM, which are those specific isomers formed from gas phase N_2O_5 and/or OH radical reactions with pyrene and fluoranthene, indicate the formation of nitroarenes during atmospheric transport from source to receptor.

Of particular note is the observation, shown in Figure IX-1, of a greatly enhanced 2-nitrofluoranthene/2-nitropyrene concentration ratio in the nighttime ambient POM sample collected at Claremont, when NO_3 radicals were observed (Biermann et al. 1988), and hence N_2O_5 was also expected to be present (Atkinson et al. 1986). Since 2-nitropyrene appears to be formed in the gas phase only from the OH radical-initiated reaction, while 2-nitrofluoranthene is formed from both the OH radical and N_2O_5 reactions, this strongly suggests that in this nighttime sample the reaction of N_2O_5 with fluoranthene was a major contributor to the 2-nitrofluoranthene observed. Thus, consistent with our laboratory data, both the N_2O_5 and OH radical-initiated reactions must be considered as possible routes to nitroarene formation in ambient atmospheres.

When ambient air was sampled with Tenax-GC solid adsorbent and PUF plugs in combination with filters, a number of more volatile nitroarenes were identified and measured (Sections VII and VIII). Thus 1- and 2-nitronaphthalene and 3-nitrobiphenyl were collected mainly on the PUF plugs, at concentrations an order of magnitude higher than 2-nitrofluoranthene. The observed ambient concentrations of 3-nitrobiphenyl, 2-nitrofluoranthene, 2-nitropyrene and 1- and 2-nitronaphthalene at Torrance (Section VIII) are consistent with those expected from the simultaneously measured parent PAH concentrations, the OH radical reaction rate constants, and our measured nitroarene formation yields (Arey et al. 1987). Thus, these ambient air measurements give further evidence for the

occurrence of atmospheric reactions of gas-phase PAH via OH radical-initiated reactions, leading to nitroarene formation.

Glendora as a Case Study of Gas-Phase PAH Reaction. Our most detailed data set for the more volatile PAH was obtained at the Glendora site, which was also characterized by a reasonably consistent pattern of photochemical air pollution during the continuous 9-day sampling period. This data set then allows the most rigorous evaluation of the occurrence of atmospheric transformations of gas-phase PAH. At this site, the ambient concentrations of the PAH exhibited significant diurnal variations, with the concentrations generally being higher during the nighttime sampling periods than during the daytime periods. This diurnal variation was most readily seen for the volatile PAH which were sampled onto the high- and low-flow Tenax cartridges and for which individual 12-hr analyses were carried out (Table VII-8). This diurnal variation could, in general, be due to differing day/night emission rates, meteorology (with lower inversion heights and hence higher concentrations during the nighttime periods) and/or differing atmospheric removal rates due to chemical reactions. The observation (see Table VII-8) that the magnitude of the diurnal variation depended on the specific PAH, with the largest variations being for the most chemically reactive PAH, indicates that part of this variation was due to chemical removal of the PAH during daytime hours.

Interestingly, the ratio (average nighttime PAH concentration/average daytime PAH concentration) varies linearly with the OH radical reaction rate constants for these PAH [which vary from $7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for biphenyl to $1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for acenaphthylene (Atkinson 1986, Atkinson and Aschmann 1988)], as shown by the plot in Figure IX-2. This relationship confirms our expectation that daytime reaction with the OH radical is an important atmospheric removal process for the PAH present in the gas phase.

The nitroarenes also exhibited a diurnal concentration profile, as shown in Figure IX-3 which gives our earlier data from Torrance (Section VIII) as well as Glendora. Again, this observed diurnal variation in the nitroarene concentrations can be due to differing emission rates, differing formation rates from their parent PAH during transport through the atmosphere, meteorology, or differing removal rates during daytime and

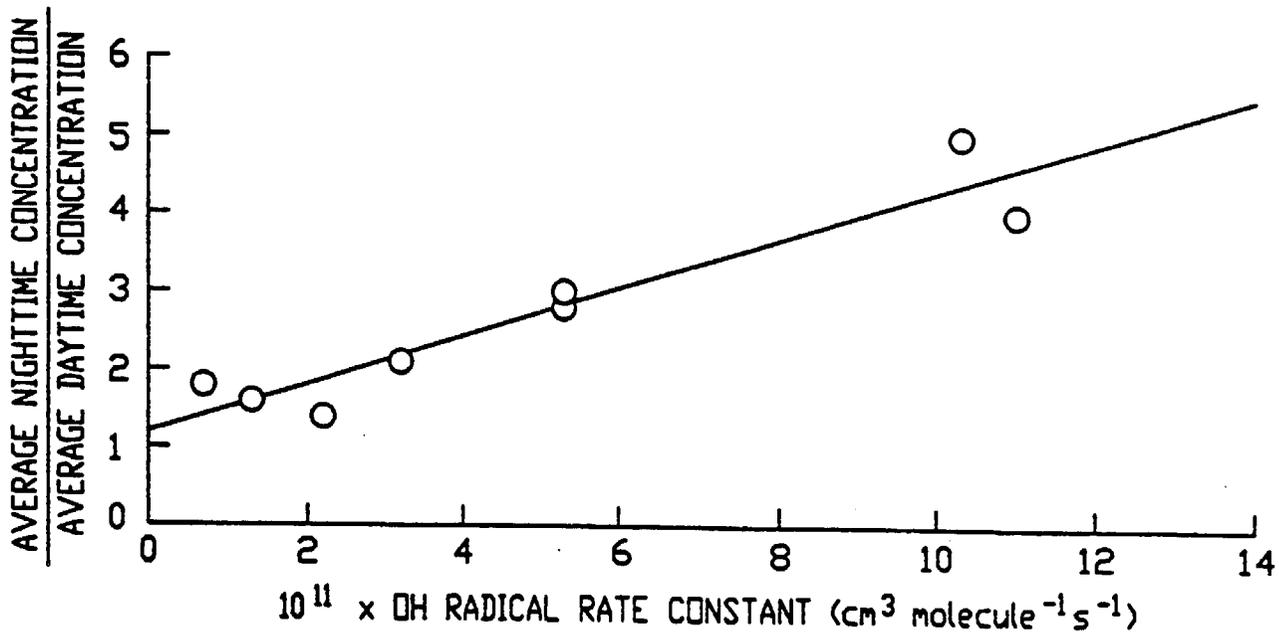


Figure IX-2. Plot of the average nighttime/average daytime concentration ratio for the volatile PAH against their OH radical reaction rate constants.

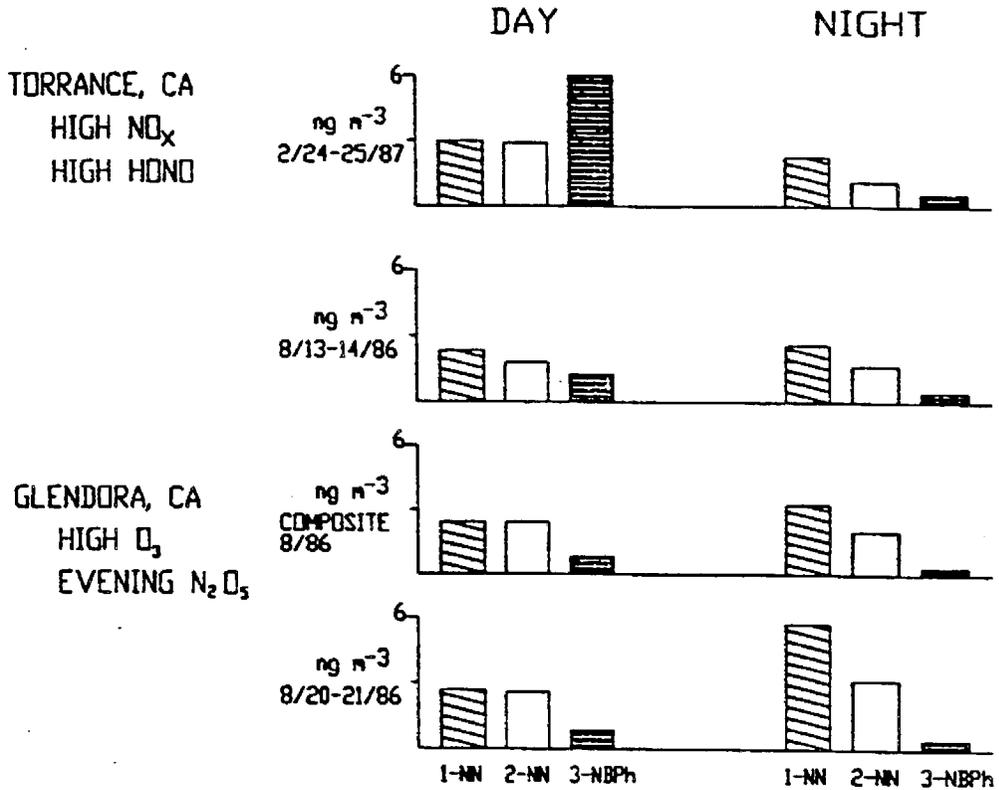


Figure IX-3. Comparison of the daytime and nighttime ambient concentrations of 1-nitronaphthalene (1-NN), 2-nitronaphthalene (2-NN) and 3-nitrobiphenyl (3-NBPh) at El Camino Community College, Torrance, CA and Citrus College, Glendora.

nighttime periods. Our data for the volatile PAH (Figure IX-2) show that meteorology at Glendora had a relatively minor effect, of the order of 20% (estimated from the intercept which represents no OH radical reaction), on the day/night concentration ratio. Further, it is expected (Atkinson et al. 1987b) that the atmospheric OH radical reactions of the nitroarenes will be relatively slow. Hence, since 3-nitrobiphenyl is not expected to be emitted and the daytime/nighttime emission rates of the nitronaphthalenes are not likely to vary significantly, the observed differences in the day/night concentration profiles for 1- and 2-nitronaphthalene and 3-nitrobiphenyl strongly suggest differing formation routes.

In particular, our observation that the daytime concentrations of 3-nitrobiphenyl at Torrance and Glendora were always higher than the nighttime concentrations (in contrast to the situation for the PAH at Glendora) shows that 3-nitrobiphenyl must be made in the atmosphere during daytime hours. Indeed, we have shown from laboratory studies (Atkinson et al. 1987b) that the daytime OH radical reaction with biphenyl (the only significant atmospheric chemical removal process for biphenyl) forms 3-nitrobiphenyl (in the presence of NO_x) in an approximately 5% yield. 1- and 2-Nitronaphthalene are also formed from the reaction of OH radicals with naphthalene (Atkinson et al. 1987b), but these nitroarenes can also be formed from the nighttime reaction of naphthalene with N_2O_5 (Atkinson et al. 1987b).

Making the assumption that the processes controlling the atmospheric concentrations of the PAH are:

	Source → PAH	R
and		
<u>daytime</u>	PAH → dilution	k_d
	OH + PAH → products	k_{OH}
<u>nighttime</u>	PAH → dilution	k_n

where R is the PAH emission rate, k_d and k_n are the daytime and nighttime dilution rates, respectively, and k_{OH} is the OH radical reaction rate

constant. Provided that the PAH emission sources do not change from daytime to nighttime, then

$$[\text{PAH}]_{\text{day}} = R / (k_d + k_{\text{OH}}[\text{OH}]) \quad (\text{I})$$

$$[\text{PAH}]_{\text{night}} = R / k_n \quad (\text{II})$$

and,

$$\frac{[\text{PAH}]_{\text{night}}}{[\text{PAH}]_{\text{day}}} = \frac{k_d}{k_n} + \frac{k_{\text{OH}}[\text{OH}]}{k_n} \quad (\text{III})$$

A plot of the nighttime/daytime concentration ratio of the PAH against their OH radical reaction rate constants [the rate constants are those measured (Table IX-2), except for fluorene for which the OH radical rate constant is calculated (Atkinson 1987)], should be a straight line of intercept k_d/k_n and slope $[\text{OH}]/k_n$, where $[\text{OH}]$ is the average 12-hr OH radical concentration. Typical plots of equation (III) are shown in Figure IX-4 for two night/day time periods [only the data for biphenyl, fluorene, naphthalene, 1- and 2-methylnaphthalene, phenanthrene and acenaphthene have been used, since acenaphthylene reacts rapidly with O_3 (Table IX-3)]. A weighted average of the 13 day/night data sets available yields a slope of,

$$\frac{[\text{OH}]}{k_n} = (4.4 \pm 1.6) \times 10^{10} \text{ molecule cm}^{-3} \text{ s}^{-1}$$

where the indicated error is two weighted least-squares standard deviations of the slopes of plots of equation (III). An essentially identical value of $[\text{OH}]/k_n$ is obtained from the low-flow Tenax cartridge data for naphthalene and 1- and 2-methylnaphthalene, with $[\text{OH}]/k_n = (5.2 \pm 4.6) \times 10^{10} \text{ molecule cm}^{-3} \text{ s}^{-1}$, where the indicated error is again two least-squares deviations.

In order to derive a value for the average 12-hr OH radical concentration from this ratio, the nighttime dilution/dispersion rate needs to be known. While previous computer modeling data indicate values of k_n of approximately $3 \times 10^{-5} \text{ s}^{-1}$ (Lurmann et al. 1986), our data for the diurnal day/night concentrations of 3-nitrobiphenyl allow values of k_n for the

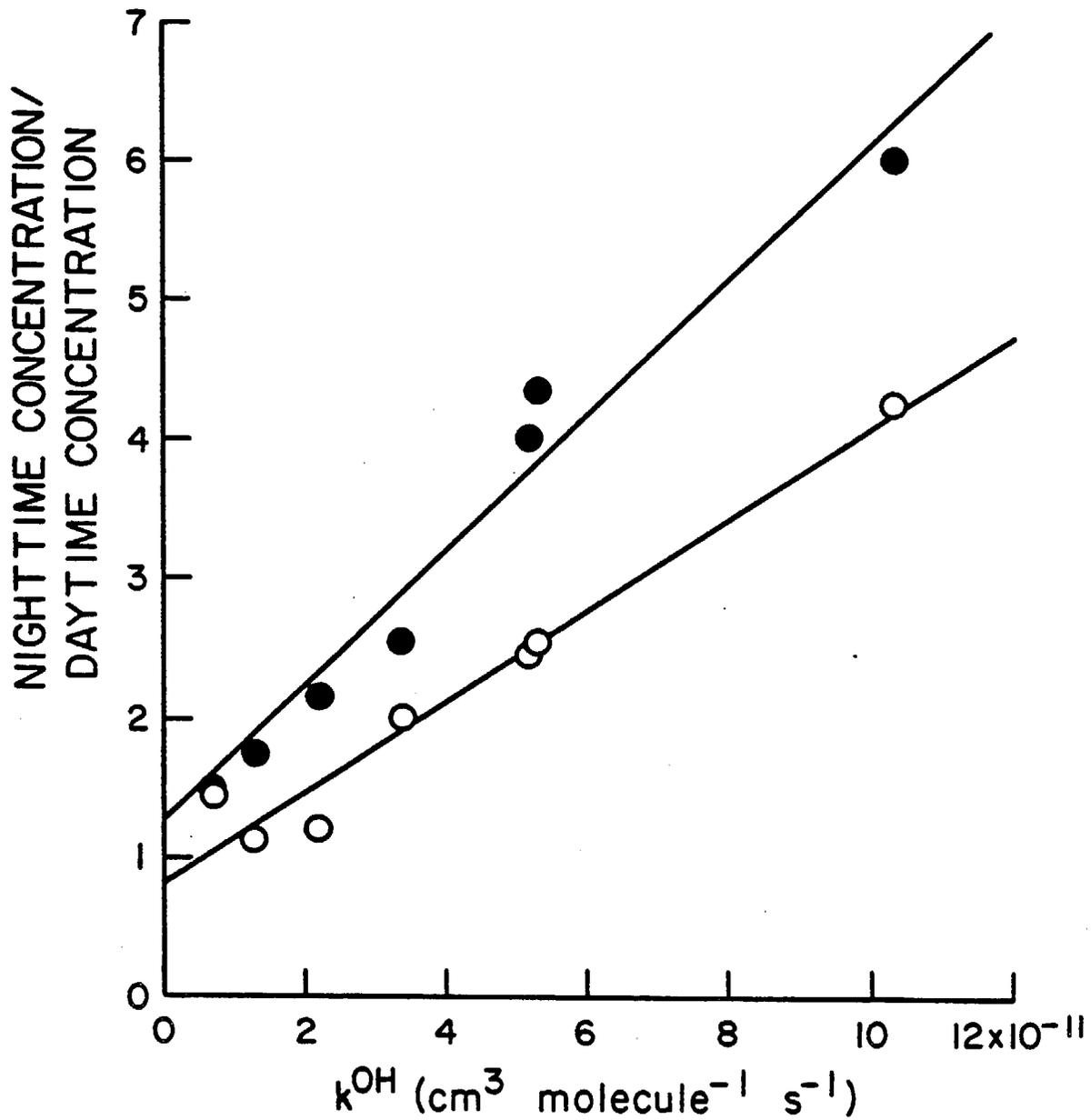


Figure IX-4. Plots of the nighttime/daytime concentration ratios for the volatile PAH against the OH radical reaction rate constant for two day/night periods at Glendora.

same time-period to be estimated. Thus, as discussed above, 3-nitro-biphenyl appears to be formed only by daytime atmospheric reaction of OH radicals with biphenyl (in the presence of NO_x), with no obvious nighttime sources. Hence, the daytime/nighttime concentration ratio of 3-nitro-biphenyl allows the nighttime dilution/dispersion rate k_n to be estimated (this argument cannot be extended to the 1- and 2-nitronaphthalenes since these nitroarenes can also be formed from the nighttime reaction of N_2O_5 with naphthalene and/or emitted).

For 3-nitrobiphenyl, the average daytime/nighttime concentration ratio is approximately given by

$$\text{ratio} = \frac{k_n t}{(1 - e^{-k_n t})} \quad (\text{IV})$$

where t is the collection time (12 hr in this case). From our observed daytime/nighttime 3-nitrobiphenyl concentration ratios, values of k_n (in units of 10^{-5} s^{-1}) of 5.9, 5.3 and 3.4 can be calculated for the day/night combinations of August 13/13-14; 15/15-16 + 16/16-17 + 17/17-18 + 18/18-19; and 20/20-21, respectively. Weighted by the number of 12-hr time periods involved, this leads to an estimated value of

$$k_n = 5 \times 10^{-5} \text{ s}^{-1},$$

consistent with expectations and in good agreement with Lurmann et al. (1986). When combined with the $[\text{OH}]/k_n$ ratio derived above, this leads to an average ambient 12-hr daytime OH radical concentration of

$$[\text{OH}] = 2 \times 10^6 \text{ molecule cm}^{-3}.$$

Due to uncertainties in the relative day/night emission rates of PAH, with these emission rates being expected, if anything, to be lower at night, and other associated uncertainties, this estimated 12-hr daytime OH radical concentration is expected to be uncertain by at least a factor of 2. This estimated summertime OH radical concentration is totally consistent with both global [which lead to a diurnally and annually averaged daytime OH radical concentration of $1.5 \times 10^6 \text{ molecule cm}^{-3}$ (Prinn et al. 1987)] and Los Angeles Air Basin modeling studies (Lurmann

et al. 1986), and constitutes an important estimate based upon the in situ time-dependent behavior of a series of organic chemicals for which the major loss process is known to be via OH radical reaction with known rate constants.

In our previous study in Torrance, CA (Arey et al. 1987), NO₃ radicals were not present during nighttime hours, and hence the N₂O₅ formation route to the 1- and 2-nitronaphthalenes was not operative, and the daytime concentrations of the 1- and 2-nitronaphthalenes and 3-nitrobiphenyl were higher than during the nighttime, as expected from a daytime formation pathway via OH radical reaction from their parent PAH. In contrast, at Glendora NO₃ radicals were observed on several evenings, and both daytime and nighttime formation of 1- and 2-nitronaphthalene was hence possible (note that 3-nitrobiphenyl could only be formed during the daytime). Indeed, while the daytime 3-nitrobiphenyl concentrations were higher than the nighttime concentrations, the 1- and 2-nitronaphthalene concentrations were as high, or higher, during the nights (Figure IX-3). Even more interesting is the observation that during daytime the 1- and 2-nitronaphthalene concentrations were comparable, consistent with the similar formation yields from the daytime OH radical-initiated reactions with naphthalene (Atkinson et al. 1987). During nighttime, however, the 1-nitronaphthalene concentrations were significantly higher than the 2-nitronaphthalene concentrations, consistent with nighttime formation from the N₂O₅ reaction with naphthalene for which the 1- and 2-nitronaphthalene yields are ~15% and 7%, respectively (Table IX-4).

In summary, it appears that only those 2-4 ring PAH present in the gas phase undergo significant amounts of reaction during atmospheric transport from source to receptor. Furthermore, the gas-phase reactions of N₂O₅ and/or OH radicals with these 2-4 ring PAH are extremely important in that they appear to produce the majority of the nitroarenes observed in ambient air.

X. DISCUSSION

In Sections IV and VII above, the experimental data on the mutagenicity of extracts of collected ambient POM and the concentrations of a series of PAH and PAH-derivatives in ambient air samples collected at seven sites throughout California have been presented. The sites at which ambient air sampling was carried out were chosen to represent areas impacted by diverse combustion emissions, as well as at varying proximity to such sources. Thus, our results provide, at least in part, the data base needed to assess the ambient levels of PAH and PAH-derivatives to which Californians are exposed and, as such, will be an important element of the data base used by the ARB in their review of the PAH as potential Toxic Air Contaminants under the AB 1807 process.

Additionally, because of the large number of PAH and PAH-derivatives for which ambient concentration data have been obtained and the large number of ambient air samples for which detailed chemical analyses were carried out (twenty-four), this data base can be used to explore relationships among the different PAH and PAH-derivatives, and between the measured mutagenicities of ambient POM extracts and the PAH and/or PAH-derivatives. In the remainder of this section, such correlations are examined and the implications of the results presented.

Data on ambient PAH concentrations, in themselves, do not allow ready conclusions to be drawn concerning source emission characteristics or PAH atmospheric transformation and removal rates. Furthermore, and an issue of great scientific and regulatory interest, we do not yet know the chemical compounds responsible for the great majority of the measured mutagenicity of collected ambient POM. However, the present data base provides a unique opportunity to examine several questions relevant to the regulatory process.

In the correlations shown below, the data from Glendora, Yuba City, Concord, Mammoth Lakes, Oildale and Reseda, but not Pt. Arguello have been used, since the ambient PAH concentrations and the POM mutagen densities at the Pt. Arguello site were uniformly low.

A. The Potential for a Readily-Monitored PAH to Serve as a Surrogate for all PAH Species

It is clear from this program that speciated PAH monitoring requires a substantial amount of time and effort, and thus the ability to use a readily-monitored PAH as a surrogate for the more complex PAH would be extremely time- and cost-effective. Among the PAH, naphthalene is present in ambient air at the highest concentrations (Section VII) and, therefore, can be relatively easily monitored. We have correlated, using our present data set, naphthalene with a number of other PAH. Figure X-1 shows plots of the naphthalene concentrations (composited to be compatible with the PUF plug and filter PAH data) against the phenanthrene and benzo[a]pyrene concentrations, while Figure X-2 shows an analogous plot of the naphthalene concentrations against those for benzo[e]pyrene. Clearly, there are large differences among the individual sites for the observed ambient air ratios of these PAH, and this is also true for correlations between naphthalene and other PAH such as fluoranthene and pyrene.

While the differing atmospheric removal rates of these PAH can give rise to differing concentration ratios in the atmosphere, the atmospheric removal rates of the PAH shown in Figures X-1 and X-2 are not expected to be rapid enough or different enough to account for the observed concentration ratio variations. Thus, benzo[e]pyrene is one of the less reactive PAH and, since it is particle-associated, is probably removed only slowly from the atmosphere. Similarly, naphthalene is the least reactive of the fused-ring PAH, with phenanthrene being only 50% more reactive towards the OH radical (the major atmospheric loss process for the gas phase PAH; see Section IX). Benzo[a]pyrene is regarded as a reactive, particle-associated, PAH (see, for example, Pitts et al. 1986 and Arey et al. 1988), and this is evident from our data, which show distinct differences among the average benzo[e]pyrene/benzo[a]pyrene concentration ratios from site to site (Table X-1) [see also below]. However, the observed reactivity of benzo[a]pyrene cannot account for the scatter shown in the plot of naphthalene against benzo[a]pyrene (Figure X-1).

Thus, the large differences observed among the concentration ratios of the PAH for these six sites strongly suggests that the PAH emission profiles differ significantly for the combustion emission sources at these sites, and that naphthalene cannot be used as a surrogate for the more complex PAH.

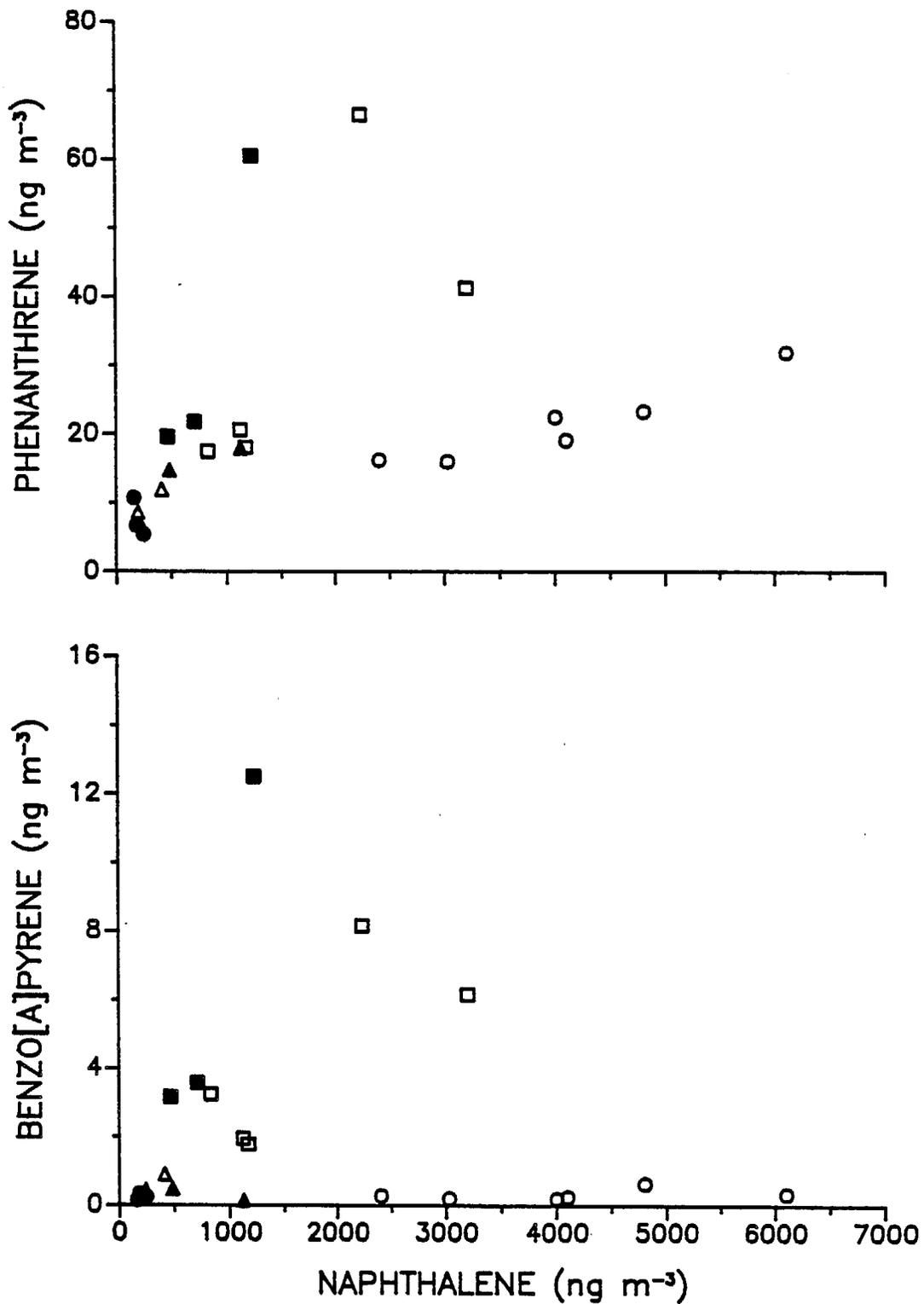


Figure X-1. Ambient concentrations of naphthalene (with the individual 12-hr data composited to be consistent with the composite PUF plug and filter sample data) plotted against those of phenanthrene (upper) and benzo[a]pyrene (lower).
 o - Glendora; ● - Yuba City; □ - Concord; ■ - Mammoth Lakes; Δ - Oildale; ▲ - Reseda.

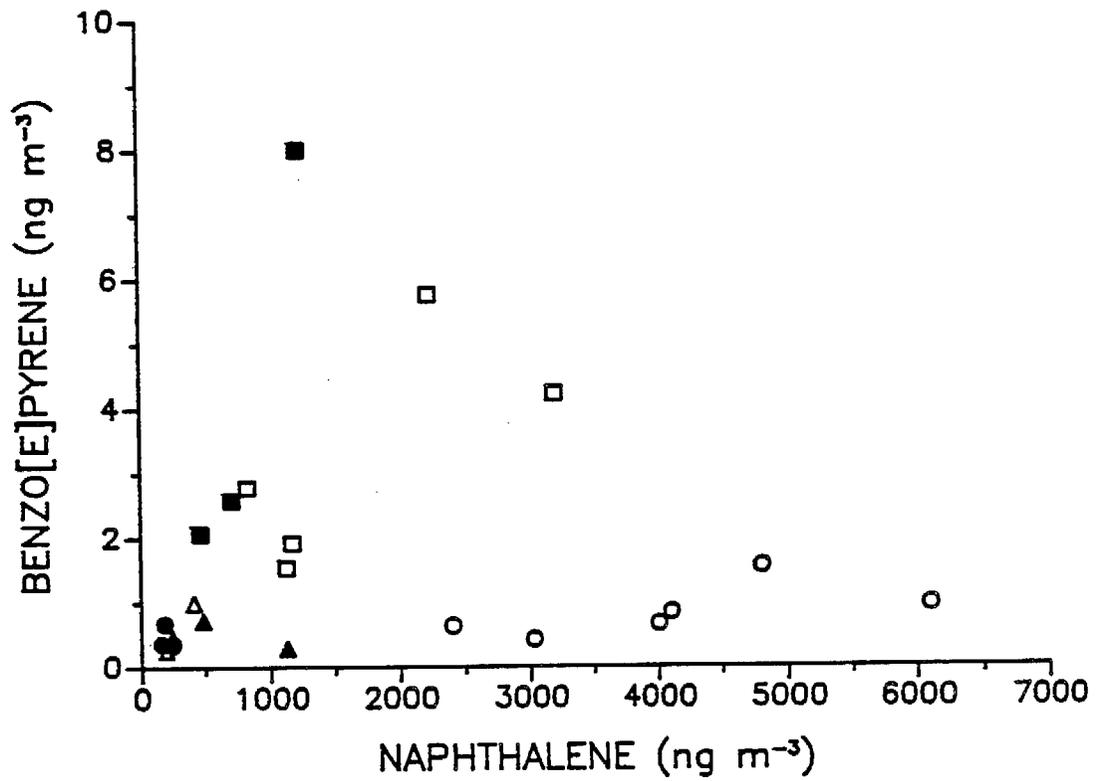


Figure X-2. Ambient concentrations of naphthalene (with the individual 12-hr data composited to be consistent with the composite filter sample data) plotted against those of benzo[e]pyrene. o - Glendora; ● - Yuba City; □ - Concord; ■ - Mammoth Lakes; Δ - Oildale; ▲ - Reseda.

Table X-1. Summary of the Average Values of Ambient PAH and PAH-Derivative Concentrations and Mutagenic Burdens at the Sites Sampled

	ng m ⁻³											rev m ⁻³			
	Naphthalene	Phenanthrene	Anthracene	Dibenzothiophene	Fluoranthene	Pyrene	BeP ^a	BaP ^a	Cyclopenta-(od)pyrene	Retene	2-NP ^a	1-NP ^a	2-NP ^a	Mutagenicity (TA98)	-S9
Glendora	3600	20	0.90	3.0	5.3	3.8	0.68	0.24	0.051	0.11	0.63	0.016	0.019	35	33
Yuba City	510	7.6	0.57	1.6	2.5	1.7	0.40	0.20	0.057	0.12	0.13	0.008	0.008	30	24
Concord	1500	34	8.1	2.7	14	12	3.4	4.4	3.8	0.88	0.29	0.030	0.050	62	63
Mammoth Lakes	780	33	10	0.72	23	22	4.1	6.2	5.9	37	0.029	0.008	0.003	7.1	22
Oildale	290	8.1	0.67	1.1	1.7	1.7	0.55	0.49	0.056	0.073	0.028	0.007	0.001	8.8	10
Reseda	810	16	1.6	1.7	4.4	3.6	0.48	0.29	0.16	0.039	0.15	0.008	0.013	22	19
Pt. Arguello	87	2.9	0.18	0.31	0.29	0.19	0.006	-	-	0.034	0.005	0.0005	0.0003	0.4	0.2
San Nicolas Island					>0.04	>0.07	0.005	-	-	0.064	0.002	0.003	-	-	-

^aBeP = Benzo[e]pyrene; BaP = benzo[a]pyrene; 2-NF = 2-nitrofluoranthene; 1-NP = 1-nitropyrene; 2-NP = 2-nitropyrene.

Figure X-3 shows plots of the phenanthrene concentrations against fluoranthene, and of fluoranthene against pyrene. It can be seen that there is an excellent correlation between the fluoranthene and pyrene concentrations, with the ambient concentrations of these PAH isomers being almost identical (see also Table X-1). This observation is consistent with prior expectations that fluoranthene and pyrene are emitted in essentially identical amounts from combustion sources (Schuetzle and Frazier 1986) and that they have very similar atmospheric lifetimes towards reaction with the OH radical [calculated using the estimation method of Biermann et al. (1985)].

There is also a correlation between the ambient phenanthrene and fluoranthene (and hence pyrene) concentrations, with the ambient ratios being reasonably constant for a specific site but varying from site to site. These trends in the fluoranthene and phenanthrene concentration ratios from site to site may be associated with the different atmospheric reactivities of these two PAH, with fluoranthene calculated to be approximately 50% more reactive than phenanthrene towards the OH radical. Similar plots of the ambient concentrations of phenanthrene against benzo[a]pyrene and benzo[e]pyrene are shown in Figure X-4. Again, significant amounts of scatter are evident in these plots and it is clear that, although a general correlation exists for phenanthrene vs. benzo[e]pyrene, good correlations exist only for closely related PAH which are present in the same phase (gas or particle) and have similar atmospheric reactivities (for example, pyrene and fluoranthene). Thus, we conclude that, except in a general sense, no one PAH can be used as a reliable surrogate for the wide range of PAH encountered in ambient air.

B. PAH as Tracers for Specific Emissions

It has been reported by Ramdahl (1983) that retene (1-methyl-7-isopropylphenanthrene) is emitted during the combustion of soft resinous wood (but not from the burning of straw or birch), and Grimmer et al. (1982) have reported that cyclopenta[cd]pyrene is a tracer for automobile emissions. We identified and quantified these two PAH in the ambient air samples collected during this study. In addition, dibenzothiophene was also identified and quantified at all sites. We have investigated the

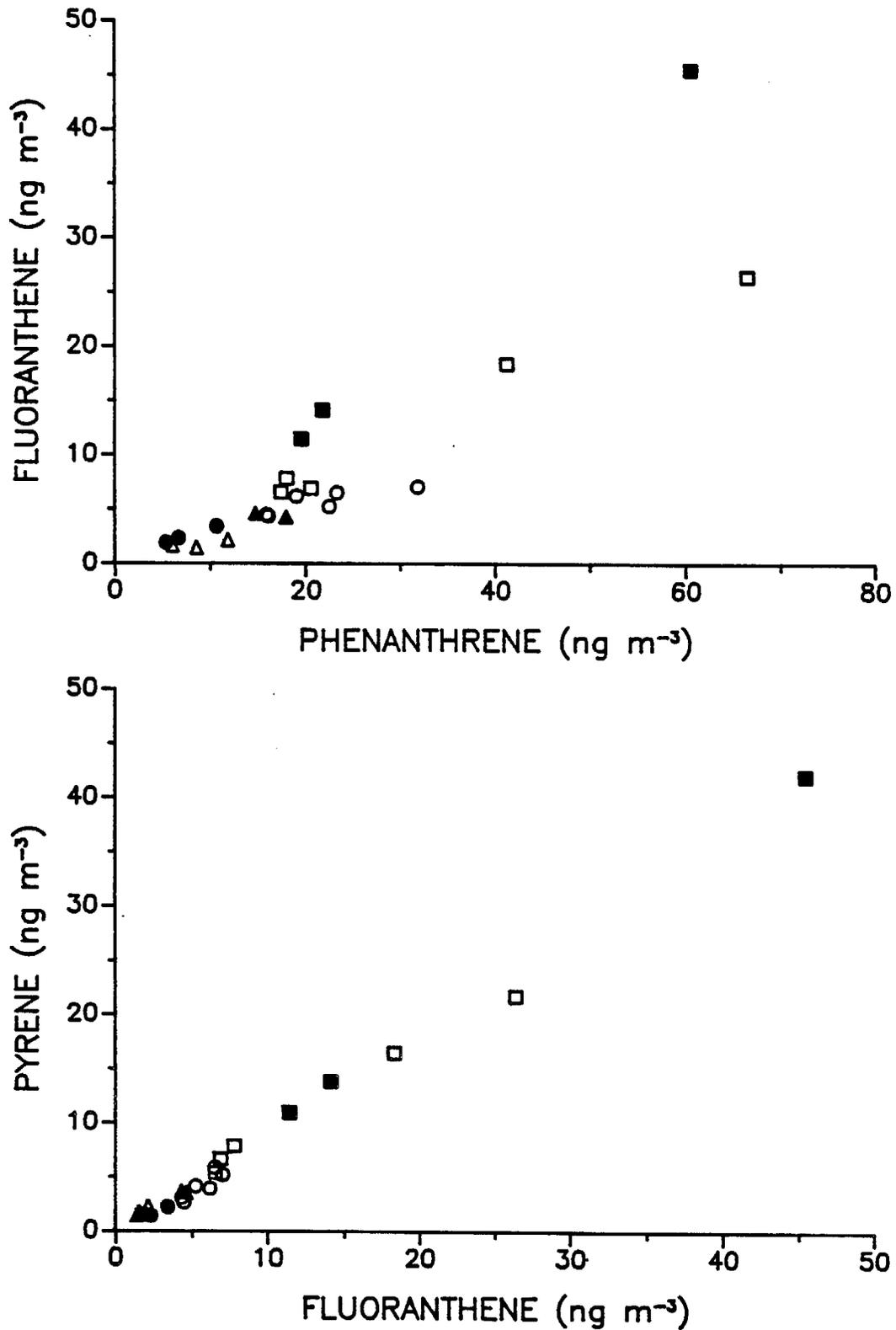


Figure X-3. Ambient phenanthrene concentrations plotted against those of fluoranthene (upper) and ambient fluoranthene concentrations plotted against those of pyrene (lower). [The fluoranthene and pyrene concentrations are the total of those observed on the PUF plugs and TIGF filters]. o - Glendora; ● - Yuba City; □ - Concord; ■ - Mammoth Lakes; △ - Oildale; ▲ - Reseda.

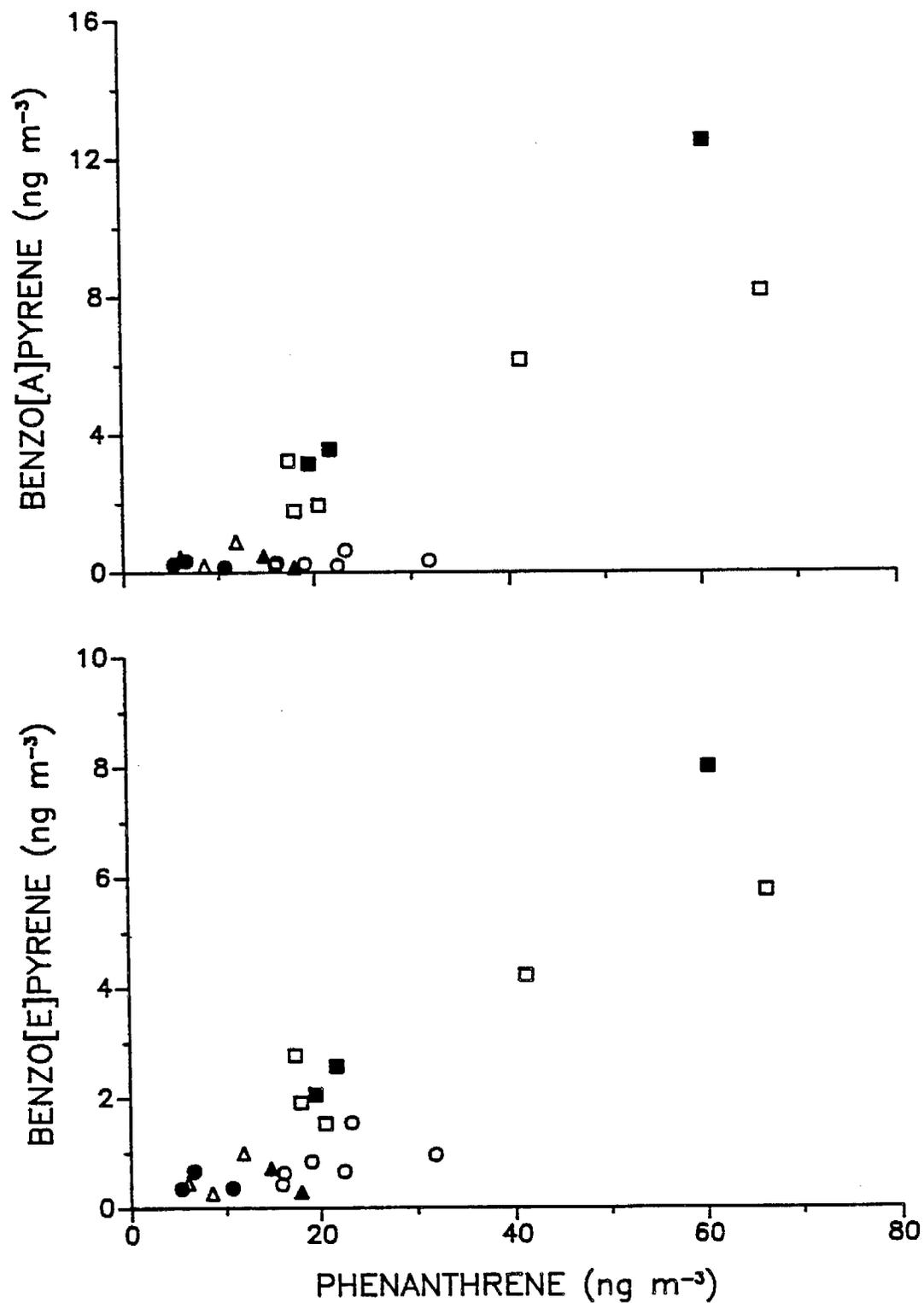


Figure X-4. Ambient phenanthrene concentrations plotted against those for benzo[a]pyrene (upper) and benzo[e]pyrene (lower).
 o - Glendora; ● - Yuba City; □ - Concord; ■ - Mammoth Lakes;
 △ - Oildale; ▲ - Reseda.

relationships between the ambient concentrations of these PAH and PASH and other PAH at each of the six sites to determine if these PAH and PASH can be used as tracer compounds for specific emission sources. Retene, an alkyl-phenanthrene, and dibenzothiophene, a PASH of similar volatility (judging from its collection on the PUF plugs) to phenanthrene are shown plotted against phenanthrene in Figure X-5. Cyclopenta[cd]pyrene is shown plotted against another particle-associated species, benzo[e]pyrene, in Figure X-6.

It is clear from Figure X-5 and Table X-1 that significant concentrations of retene were observed only at Mammoth Lakes and Concord, and that for two out of three of the composited samples at Mammoth Lakes the retene concentrations were actually higher than the phenanthrene concentrations. Retene is clearly a good indicator of PAH emissions from wood combustion, and the low levels observed at Concord (relative to Mammoth Lakes) can be ascribed to a small contribution of wood combustion emissions to the PAH collected in the Concord Samples #3 and #4. This is consistent with both of these Concord samples being collected during nighttime, with an odor of wood smoke having been noted for those nighttime samples composited into Sample #3 (Section V). In agreement with the findings of Ramdahl (1983), retene does not appear to be emitted from agricultural burning, since only very low levels of retene were measured at Yuba City.

Analogous to the situation for retene, cyclopenta[cd]pyrene was observed in highest concentrations at Concord and Mammoth Lakes (Figure X-6), although in this case the concentrations at Concord were comparable to those at Mammoth Lakes. As shown in Figure X-6, the cyclopenta[cd]pyrene/benzo[e]pyrene concentration ratios at Concord and Mammoth Lakes were similar, with these two sites having higher concentrations of these (and other) PAH than the other sites sampled. However, the expected atmospheric reactivity of cyclopenta[cd]pyrene (which may be responsible for the low concentrations observed at Glendora, Yuba City, Oildale and Reseda), and the fact that the wood burning site (Mammoth Lakes) is not distinguished from Concord on the basis of the cyclopenta[cd]pyrene levels or the cyclopenta[cd]pyrene/benzo[e]pyrene concentration ratios, leads us to conclude that cyclopenta[cd]pyrene is not a useful tracer for automobile emissions.

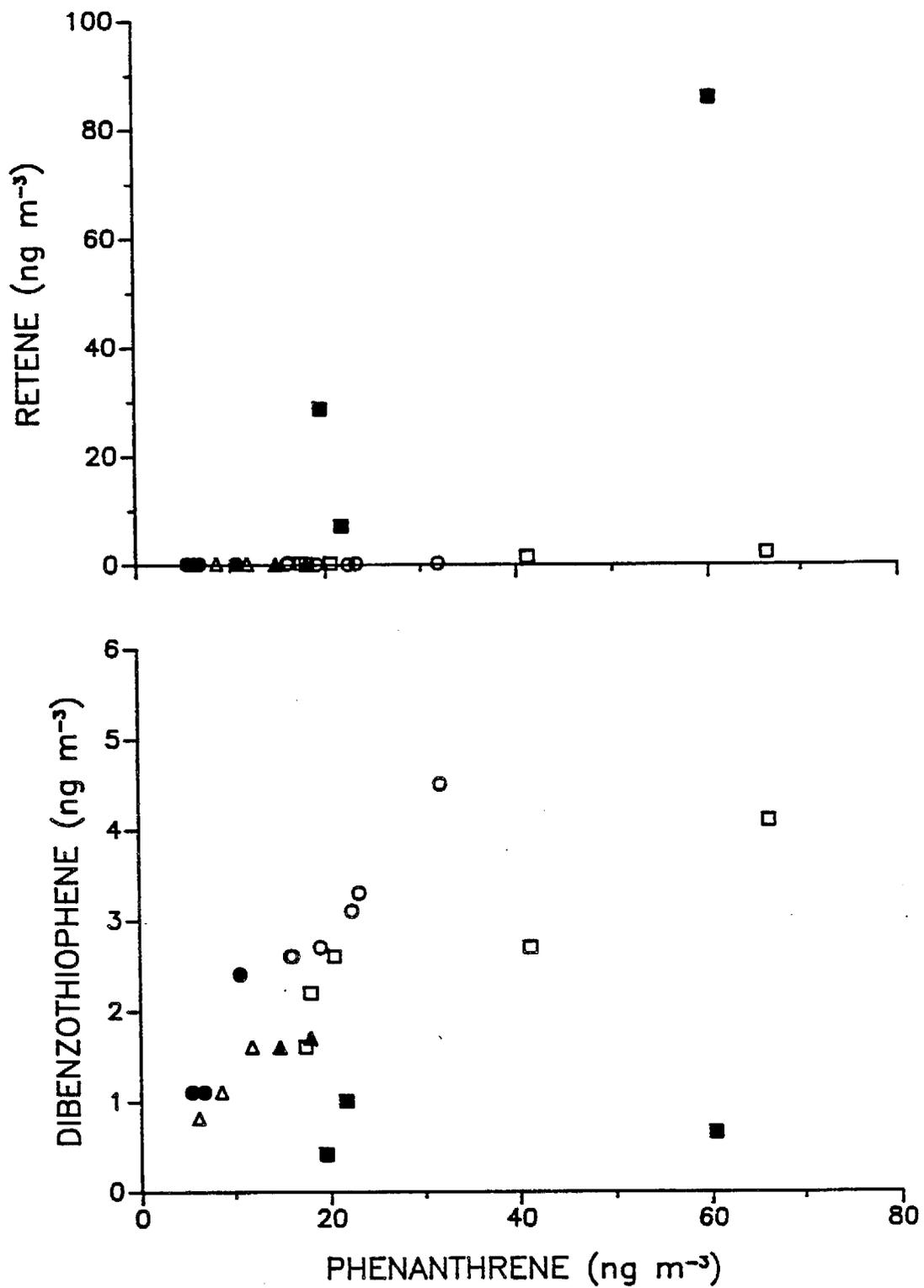


Figure X-5. Ambient concentrations of phenanthrene plotted against those of retene (upper) and dibenzothiophene (lower). o - Glendora; ● - Yuba City; □ - Concord; ■ - Mammoth Lakes; Δ - Oildale; ▲ - Reseda.

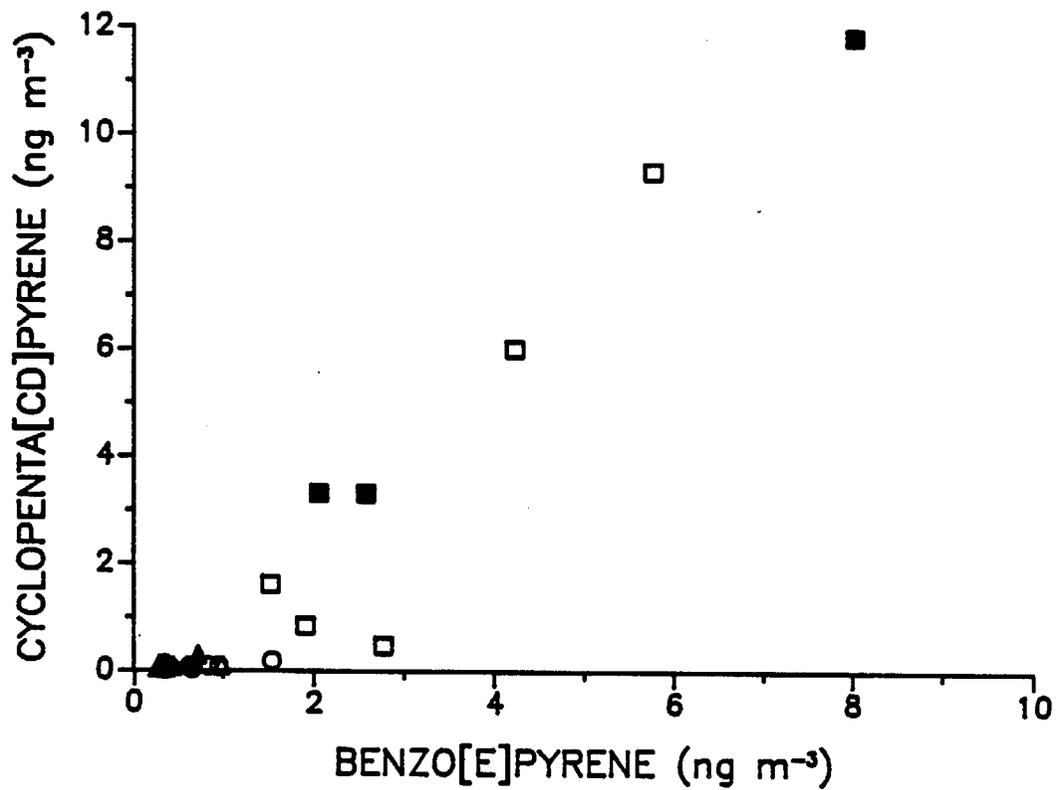


Figure X-6. Ambient concentrations of benzo[e]pyrene plotted against those of cyclopenta[cd]pyrene. o - Glendora; ● - Yuba City; □ - Concord; ■ - Mammoth Lakes; Δ - Oildale; ▲ - Reseda.

Dibenzothiophene was present at all of the seven sites. By comparing the ambient levels of dibenzothiophene vs. those of phenanthrene (Figure X-6), it appears that dibenzothiophene is emitted in lower amounts from wood combustion than from the other combustion sources encountered in this study. The generally reasonable correlation evident from the data obtained at Glendora, Yuba City, Concord, Oildale and Reseda implies that dibenzothiophene cannot be viewed as a marker for a specific combustion source.

C. Degree of Transformations of PAH in the Atmospheres Sampled

Based upon our current knowledge of the atmospheric reactions of the gas-phase PAH (Section IX), it is expected that those PAH which exist, at least partially, in the gas phase will be transformed during their transport through the atmosphere, and that the atmospheric lifetimes of the 2-4 ring PAH such as naphthalene, phenanthrene, anthracene, fluoranthene and pyrene will be of the order of 1-8 hrs during daylight [for an average 12-hr OH radical concentration of 1.5×10^6 molecule cm^{-3} (Prinn et al. 1987)]. The case study of Glendora, for which 12-hr samples of a series of volatile PAH species over an extended period were available, has been discussed in detail in Section IX, and these ambient data have been shown to be totally consistent with the expected OH radical reactions of these PAH.

Similar, though less extensive, data are available for the less volatile PAH collected on the PUF plugs demonstrating the occurrence of atmospheric transformations of these PAH. Further, the extent of atmospheric transformation of these PAH can be used to develop a relative ranking of the degree of atmospheric reaction which had occurred at the different sampling sites. For example, as been discussed above, fluoranthene and pyrene, PAH of similar reactivity, are well correlated at all sites, while fluoranthene (or pyrene) and phenanthrene are well correlated at a given site but not for all sites taken together. Thus, comparing in Figure X-3 the line formed by the Mammoth Lakes data with that formed by the Glendora data suggests that more reaction had occurred at Glendora, thereby decreasing the fluoranthene/phenanthrene ratios. A further example concerns the concentration ratios of anthracene and phenanthrene, with anthracene reacting with the OH radical a factor of

approximately 4 faster than does phenanthrene. Figure X-7 and Table X-1 show that the anthracene/phenanthrene ratio decreases in the order Mammoth Lakes > Concord > Yuba City ~ Oildale ~ Reseda > Glendora. In the absence of differing emission ratios of these isomeric 3-ring PAH, this order reflects increasing fractions of reaction which occurred during transport of these two PAH from source to sampler. This ranking applies for the variations in the phenanthrene/fluoranthene or phenanthrene/pyrene and benzo[e]pyrene/benzo[a]pyrene ratios throughout the sites sampled (see Table X-1 and Figure X-3). Interestingly, although the benzopyrenes are particle-associated, the use of phenanthrene/anthracene and benzo[e]pyrene/benzo[a]pyrene concentration ratios for judging reaction are essentially equivalent since, as shown in Figure X-8, these ratios correlate well.

We have shown in Section IX that 2-nitropyrene and 8-nitrofluoranthene are both expected to be formed in the atmosphere only by reaction of their parent PAH with the OH radical, while 2-nitrofluoranthene can be formed by both OH radical and N_2O_5 reaction with gaseous fluoranthene. Furthermore, these nitroarenes are not expected to be directly emitted, in contrast to 1-nitropyrene which is a direct emission and is not formed in the atmosphere from the gas-phase reactions of pyrene. Consistent with these conclusions, the ambient levels of 8-nitrofluoranthene correlate very well with those of 2-nitropyrene (Figure X-9), especially considering the low concentrations of both of these nitroarenes.

As we have noted above, in addition to being formed by OH radical reaction, 2-nitrofluoranthene can be formed during evening hours by the gas-phase reaction of fluoranthene with N_2O_5 . Consistent with NO_3 radicals, which are in equilibrium with NO_2 and N_2O_5 , being observed at Glendora on certain evenings, a plot of the 2-nitrofluoranthene concentrations against those of 2-nitropyrene (Figure X-12) shows elevated levels of 2-nitrofluoranthene (over those calculated from the 2-nitropyrene concentrations if only OH radical reaction is assumed) at Glendora.

Thus, our data set for the ambient concentrations of the PAH and PAH-derivatives is reasonably consistent with our understanding of the atmospheric chemistry of these compounds. These data indicate a ranking of the sites with respect to the fraction of PAH reacted during transport from sources to samplers increased in the order Mammoth Lakes < Concord

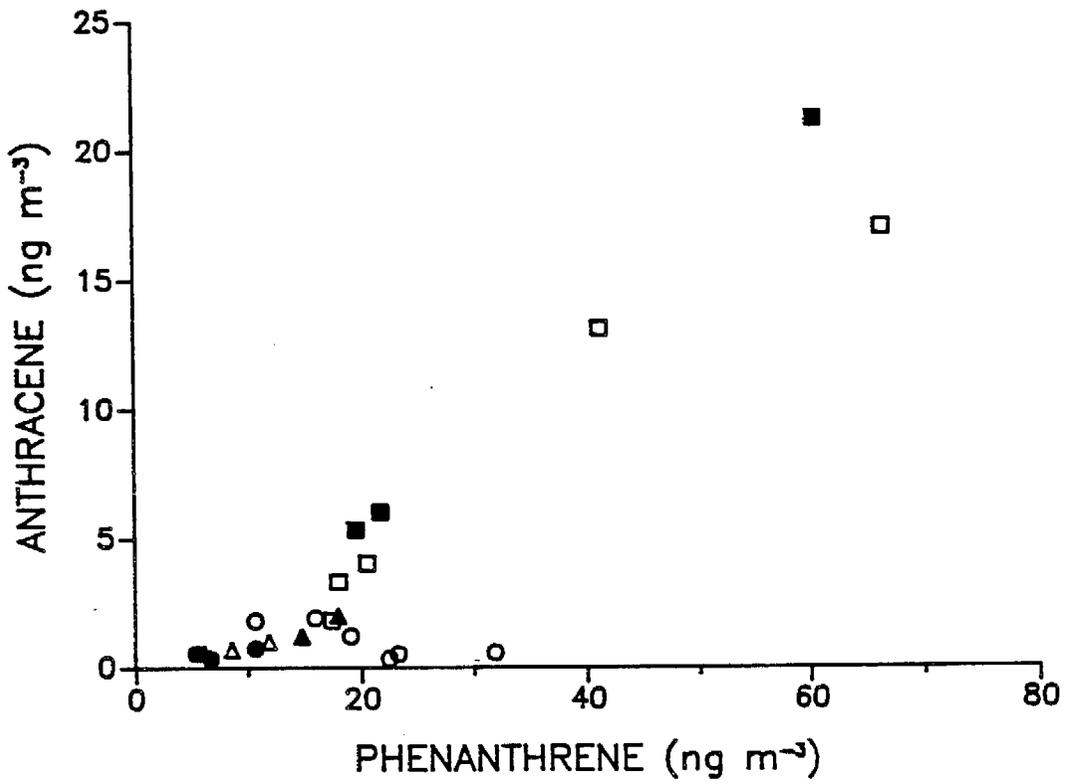


Figure X-7. Ambient concentrations of phenanthrene plotted against those of anthracene. o - Glendora; ● - Yuba City; □ - Concord; ■ - Mammoth Lakes; △ - Oildale; ▲ - Reseda.

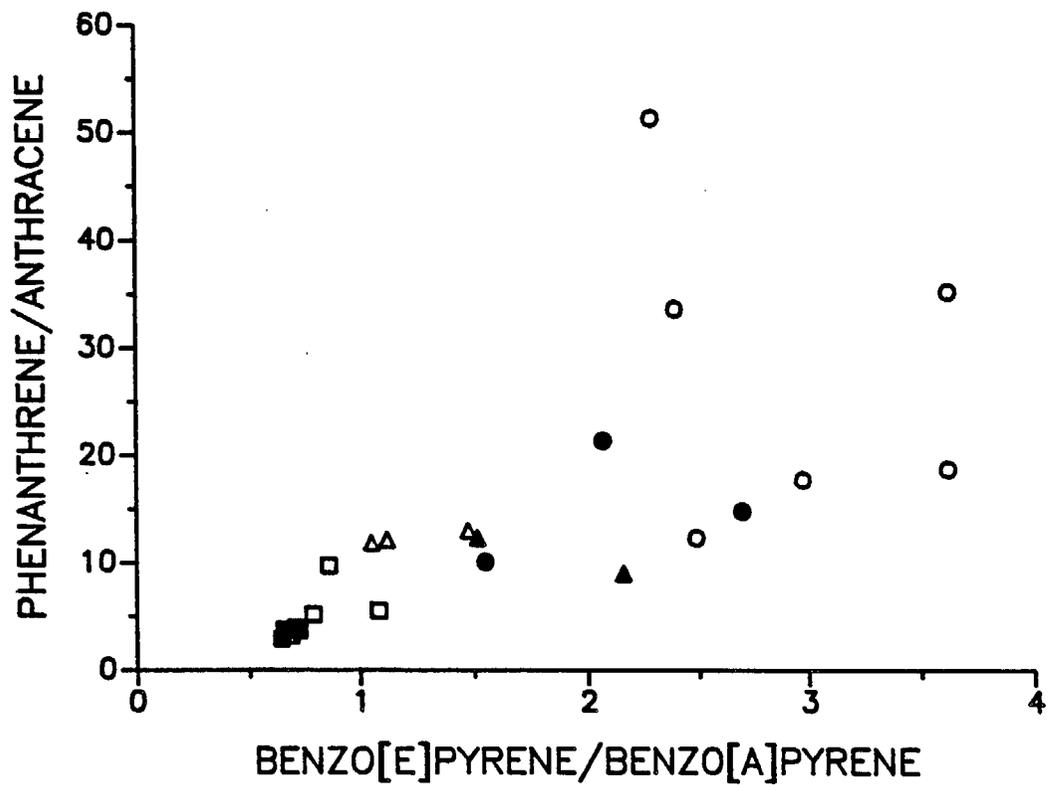


Figure X-8. The ambient phenanthrene/anthracene concentration ratios plotted against the benzo[e]pyrene/benzo[a]pyrene concentration ratio. o - Glendora; ● - Yuba City; □ - Concord; ■ - Mammoth Lakes; △ - Oildale; ▲ - Reseda.

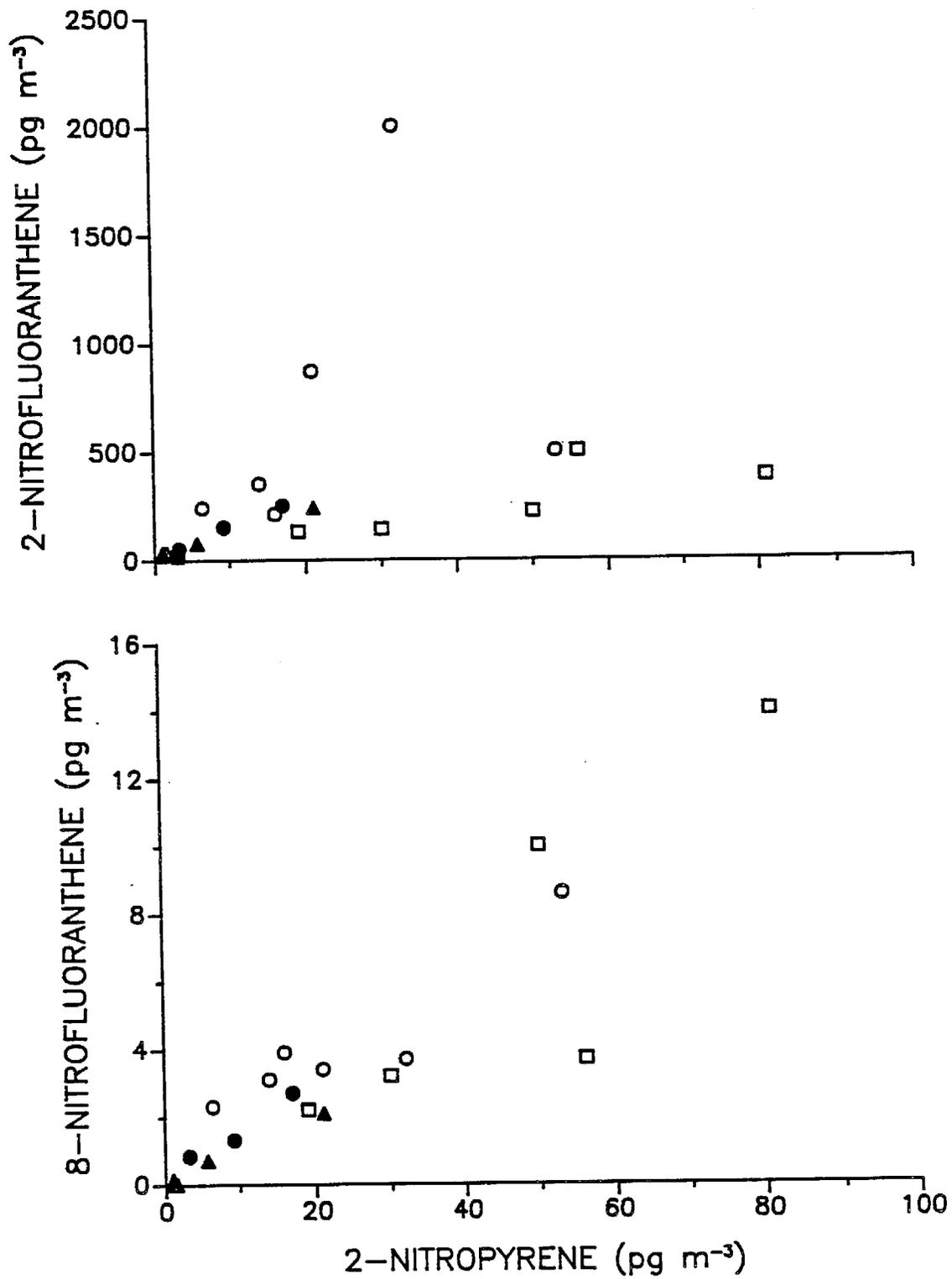


Figure X-9. Ambient concentrations of 2-nitropyrene plotted against those of 2-nitrofluoranthene (upper) and 8-nitrofluoranthene (lower). o - Glendora; ● - Yuba City; □ - Concord; ■ - Mammoth Lakes; ▲ - Oildale; ▲ - Reseda.

< Yuba City ~ Oildale ~ Reseda < Glendora. However, in terms of the amounts of reaction products expected to be encountered at these sites, the magnitudes of the PAH concentrations and/or emission strengths also need to be taken into account. The data given in Section VII and summarized in Table X-1 indicate that the ambient PAH concentrations increase in the order Pt. Arguello < Oildale < Yuba City < Reseda < Glendora < Concord ~ Mammoth Lakes. Since these two rankings are significantly different, the overall amount of reaction product formation in the atmospheres at the sites sampled cannot readily be estimated solely from these two rankings. However, the amounts of 2-nitropyrene formed (with, as noted above, 2-nitropyrene being formed only by OH radical reaction) leads to the ranking Pt. Arguello < Oildale < Mammoth Lakes < Yuba City < Reseda < Glendora < Concord in terms of the amounts of OH radical reaction products sampled.

The daily maximum O_3 and NO_x concentrations and the daily maximum and minimum temperatures encountered at the seven sampling sites are given in Table X-2. These co-pollutant and temperature data further substantiate the above reaction product ranking. Thus, at Mammoth Lakes the low NO_x levels lead to a high hydrocarbon-to- NO_x ratio expected to result in low OH radical concentrations. The low temperatures and low ozone maxima are also consistent with minimal PAH transformations. The generally clean atmospheres of Pt. Arguello and Oildale resulted in low concentrations of both PAH and PAH reaction products. At the opposite extreme, the high O_3 , high NO_x and high temperatures at Glendora would result in reaction products from O_3 , N_2O_5 , and OH radical reaction. The high PAH emissions at Concord and high ambient NO_x concentrations are similar to the conditions we encountered previously at Torrance, CA, during our January and February 1986 study. At Torrance, the high early morning HONO concentrations undoubtedly resulted in high morning OH radical concentrations.

Another interesting observation was the presence of the highly reactive PAH such as acenaphthene, acenaphthylene, acephenanthrylene and cyclopenta[cd]pyrene at Concord and Mammoth Lakes, which were characterized by high ambient PAH concentrations and/or low atmospheric reactivities.

Table X-2. Daily Maximum O₃ and NO_x Concentrations (ppb)^a and Temperature Maxima and Minima for the Seven Sampling Sites in California

Location Sites and Dates	Maximum O ₃ Concentration (ppb)	Maximum NO _x Concentration (ppb)	Temperature			
			Maximum		Minimum	
			°C	°F	°C	°F
<u>Glendora</u>						
8/13/86	160	150	31 ^b	88	15 ^b	59
8/14/86	210	120	32	89	16	60
8/15/86	210	120	31	88	14	58
8/16/86	220	110	32	89	14	57
8/17/86	240	90 ^c	37	98	15	59
8/18/86	220	120	38	101	19	67
8/19/86	230	70	38	100	22	71
8/20/86	220	220	38	100	23	73
8/21/86	60 ^c	120 ^c	36	97	22	71
<u>Yuba City</u>						
10/16/86	70	d	29 ^e	84	9 ^e	49
10/17/86	50	d	23	73	11	51
10/18/86	40	d	23	74	8	46
10/19/86	50	d	23	74	8	46
10/20/86	110	d	26	78	9	49
10/21/86	70	d	24	75	9	49
10/22/86	60 ^c	d	26	79	9	49
10/23/86	70	d	27	81	11	51
10/24/86	50	d	21	69	12	54
10/25/86	60	d	23	74	11	52
<u>Concord</u>						
12/6/86	30 ^c	130 ^c	17 ^f	63	7 ^f	45
12/7/86	40	200	17	63	7	45
12/8/86	30	400	14	57	3	37
12/9/86	40	230	16	61	3	37
12/10/86	10	180	9	48	1	34
12/11/86	<10	70	6	43	3	37
12/12/86	10	60	6	43	4	39
1/13/87	40	160	15	59	1	34
1/14/87	40	300	20	68	2	36
1/15/87	40 ^c	<10 ^c	9	48	4	39
1/17/87	40	220	17	63	4	39
1/18/87	40	180	12	54	-1	30
1/19/87	40	290	18	64	1	34
1/21/87	60	160	16	61	1	34
1/22/87	30	280 ^c	11	52	3	37

(continued)

Table X-2 (continued) - 2

Location Sites and Dates	Maximum O ₃ Concentration (ppb)	Maximum NO _x Concentration (ppb)	Temperature			
			Maximum		Minimum	
			°C	°F	°C	°F
<u>Mammoth Lakes</u>						
2/14/87	50	50	12 ^g	54	-9 ^g	16
2/15/87	40	30	0	32	-13	8
2/16/87	40	30	1	33	-10	14
2/17/87	40	30	3	37	-8	17
2/18/87	40 ^c	20 ^c	2	28	d	d
2/20/87	50 ^c	20	4	40	d	d
2/21/87	50	30	d	d	-8	17
2/22/87	50	20	-2	28	d	d
2/23/87	40 ^c	10 ^c	0	32	d	d
2/25/87	40 ^c	<10 ^c	-8	17	-17	2
2/26/87	50	20	-6	21	d	d
2/27/87	40	30	7	45	-9	15
2/28/87	40	40	d	d	d	d
3/1/87	40 ^c	20 ^c	d	d	d	d
<u>Oildale</u>						
3/29/87	50	40	27 ^h	81	6 ^h	42
3/30/87	70	40	28	83	8	46
3/31/87	60	120	28	83	7	45
4/1/87	70	50	28	82	9	48
4/2/87	110	30	26	78	8	47
4/7/87	60 ^c	50	25	77	9	48
4/8/87	70	70	27	80	10	50
4/9/87	70	80	29	84	12	54
4/10/87	70	60	31	87	14	57
4/11/87	40	50	23	73	9	49
<u>Reseda</u>						
5/27/87	80	70	21 ⁱ	70	7 ⁱ	44
5/28/87	70	110	27	80	7	44
5/29/87	70	130	28	82	8	46
5/30/87	100	140	32	90	9	48
5/31/87	110	160	34	93	11	51
6/1/87	110	180	36	97	10	50
6/2/87	110	160	38	100	11	52
6/3/87	150	100	39	103	12	54
6/14/87	90	60	30	86	12	53
6/15/87	50	60	30	86	9	48

(continued)

Table X-2 (continued) - 3

Location Sites and Dates	Maximum O ₃ Concentration (ppb)	Maximum NO _x Concentration (ppb)	Temperature			
			Maximum		Minimum	
			°C	°F	°C	°F
<u>Pt. Arguello</u>						
7/4/87	40	<10	24 ^J	75	13 ^J	55
7/5/87	30	<10	23	73	13	55
7/6/87	40	<10	22	72	13	55
7/7/87	40	<10	24	75	13	56
7/8/87	30	<10	21	70	13	55
7/9/87	40	<10	26	78	13	56
7/10/87	40	<10	24	75	14	57
7/11/87	40	<10	24	75	15	59
7/12/87	40	<10	26	78	11	51

^aSee Appendix D for detailed co-pollutant data.

^bValues as measured by the National Weather Service, Pasadena Station.

^cIncomplete data set.

^dNo data available.

^eValues as measured by the National Weather Service, Marysville Station.

^fValues as measured by the University of California, Davis at the Campbell Scientific Meteorological Station in Concord, CA.

^gValues as measured by SAPRC personnel, Mammoth Lakes, CA.

^hValues as measured by the National Weather Service, Bakersfield Station.

ⁱValues as measured by the National Weather Service, Canoga Park Station.

^jValues as measured by the National Weather Service, Lompoc Station.

D. Correlation of Mutagenicity and PAH

Ambient POM is a complex chemical mixture, and its mutagenic activity is almost certainly due to the presence of hundreds, if not thousands, of mutagenically-active chemical compounds, all having differing biological activities. At the present time, the plethora of chemical compounds responsible for this mutagenicity are not known. Therefore, we explored whether any of the PAH or PAH-derivatives measured in the present study showed any correlation with the ambient POM mutagenicity. The PAH concentrations did not correlate well with ambient mutagenicity, either the direct-acting mutagenicity or the mutagenicity in the presence of S9 (note that only for Mammoth Lakes was the ratio [mutagenicity to TA98 (-S9)]/[mutagenicity to TA98 (+S9)] significantly different from unity). As an example, Figure X-10 shows a plot of the ambient mutagenicity (TA98, -S9) against the naphthalene concentrations; clearly no useful correlation exists.

The best correlation between mutagenicity and PAH or PAH-derivatives was with 2-nitropyrene (Figure X-11). Although a fair degree of scatter is evident in this figure, in part due to the low levels of 2-nitropyrene and the difficulties in its measurement, the scatter (unlike that in Figure X-10 for naphthalene vs mutagen density) appears to be random and not site dependent. That is, no marked differences in the proportionality constant exist from site to site. Although circumstantial, this observation suggests that the major fraction of the measured ambient POM mutagenicity (TA98, -S9) is due to the atmospheric reaction products of primary emissions. If so, this leads to the conclusion that the direct-acting mutagenicity is a measure of the amount of atmospheric transformation products present in the POM.

E. Contribution of PAH and PAH-Derivatives to Ambient Direct-Acting Mutagenicity

Since the PAH require microsomal activation, they do not contribute to the measured direct-acting mutagenicity of ambient POM. Indeed, the only PAH and PAH-derivatives identified and quantified in this study which contributed to the ambient POM direct-acting mutagenicity were the particle-associated nitroarenes.

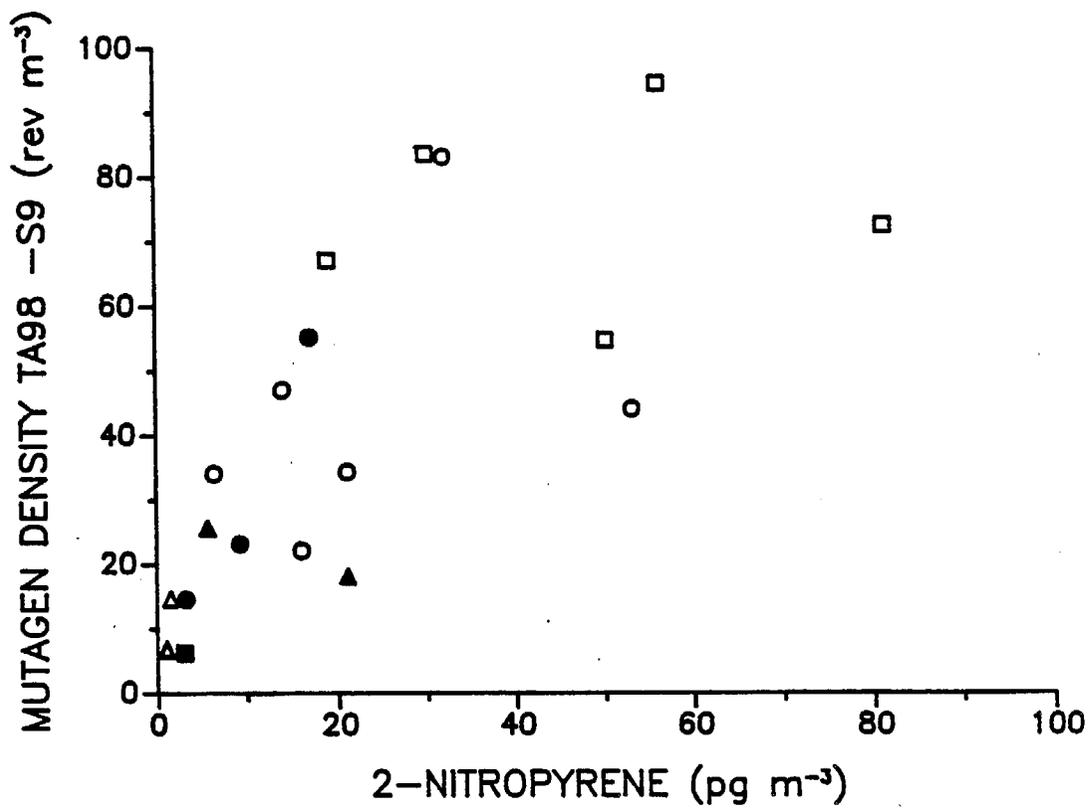


Figure X-11. Ambient concentrations of 2-nitropyrene plotted against the POM mutagenic density [strain TA98, -S9; composited (see Table X-3) to be consistent with the filter samples].
 ● - Glendora; ○ - Yuba City; □ - Concord; ■ - Mammoth Lakes;
 ▲ - Oildale; △ - Reseda.

Since the most abundant nitroarenes collected on the filters were generally the nitrofluoranthenes and nitropyrenes and, as noted in Section VII, the high 9-nitroanthracene concentrations in certain Concord samples would not contribute significantly to the ambient mutagen density, we have calculated the mutagen density due to these M.W. 247 nitroarenes. Table X-2 gives the mutagen density (strain TA98, -S9) due to 2-nitrofluoranthene, 8-nitrofluoranthene, 1-nitropyrene and 2-nitropyrene in the samples collected at each of the seven sites. It can be seen that the total mutagen density due to these nitroarenes is typically 0.1-4 revertants per m^3 , with Glendora Sample #6 being significantly higher at 9 rev m^{-3} . The observed mutagen densities (TA98, -S9), composited to be consistent with the composite filter samples, are also given in Table X-3.

It can be seen from these data that the M.W. 247 nitroarenes together contribute no more than ~10% and generally $\leq 5\%$ of the measured ambient POM mutagen density. The observation that the nitroarenes make only a small contribution to ambient POM mutagenicity, together with the evidence, discussed above, that the ambient direct-acting mutagenicity of POM is due to reaction products formed in the atmosphere leads us to expect that the $\geq 90\%$ of ambient POM mutagen density not presently accounted for is due, at least in part, to more polar PAH reaction products. Indeed, in our environmental chamber product studies of the OH radical-initiated reactions of gaseous PAH, the more polar products such as hydroxy- and hydroxynitro-PAH are significantly more abundant than the nitroarenes, and the same situation is expected to occur in the ambient atmosphere.

Table X-3. Direct-Acting Mutagenic Densities (Salmonella Strain TA98, -S9) Due to the Nitro-arenes of M.W. 247^a, Together with the Measured Ambient POM Mutagen Densities

Site	Sample #	Ambient Mutagen Density (rev m ⁻³)					Total	POM Mutagen Densities (rev m ⁻³)
		2-Nitro-fluor-anthene	8-Nitro-fluor-anthene	1-Nitro-pyrene	2-Nitro-pyrene			
Glendora	1	0.88	0.29	0.060	0.26	1.5	22	
	2	2.1	0.64	0.085	0.85	3.7	44	
	3	1.0	0.17	0.025	0.10	1.3	34	
	4	3.7	0.25	0.032	0.34	4.3	34	
	5	1.5	0.23	0.035	0.22	2.0	47	
	6	8.4	0.27	0.035	0.51	9.2	83	
Yuba City	1	0.22	0.061	0.016	0.051	0.35	14	
	2	1.1	0.20	0.032	0.27	1.6	55	
	3	0.63	0.096	0.014	0.15	0.89	23	
Concord	1	0.59	0.24	0.060	0.48	1.4	83	
	2	2.1	0.27	0.044	0.90	3.3	94	
	3	0.92	0.74	0.094	0.80	2.6	55	
	4	1.6	1.0	0.10	1.3	4.0	72	
	5	0.55	0.16	0.032	0.30	1.0	67	
Mammoth Lakes	1	0.071	nd	0.019	0.048	0.14	6.1	
	2	0.24	nd	0	nd	0.24	11	
	3	0.059	nd	0	nd	0.059	4.3	
Oildale	1	0.092	0.0096	0.012	0.016	0.13	6.8	
	2	0.15	0	0.011	0.016	0.18	6.6	
	3	0.16	0	0.025	0.024	0.21	15	

(continued)

Table X-3 (continued) - 2

Site	Sample #	Ambient Mutagen Density (rev m ⁻³)				Total	POM Mutagen Densities (rev m ⁻³)
		2-Nitro-fluor-anthene	8-Nitro-fluor-anthene	1-Nitro-pyrene	2-Nitro-pyrene		
Reseda	1	1.0	0.16	0.025	0.34	1.5	18
	2	0.33	0.053	0.012	0.090	0.49	26
Pt. Arguello	1	0.015	0	0.0015	0.0046	0.021	0.41
	2	0.024	0	0.0008	0	0.025	0.41

aDirect mutagenicity of standard nitroarenes toward TA98(-S9): 2-nitrofluoranthene, 4,200 rev μg⁻¹; 8-nitrofluoranthene, 74,000 rev μg⁻¹; 1-nitropyrene, 2,300 rev μg⁻¹; 2-nitropyrene, 16,000 rev μg⁻¹.

XI. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

The goals of this program were successfully accomplished. Ambient air samples were collected for a total of 118 12-hr periods at seven locations throughout California impacted by differing combustion emission sources, and these ambient air samples were subjected to chemical analysis and mutagenicity testing. In addition, ambient POM was collected at a background site during the SCAQS for chemical analysis. The PAH and PAH-derivatives given in Table XI-1 were identified and quantified in these ambient air samples. For naphthalene, ambient concentrations were measured for 118 12-hr periods, while for the less volatile PAH and PAH-derivatives, 24 data sets are available from composited PUF plug and TIGF filter samples, together with an additional data set from the San Nicolas Island composite filter sample. Mutagenicity testing of 98 POM samples collected over 12-hr periods, plus 4 composited samples, was carried out using strains TA98 (with and without S9) and TA98NR and TA98/1,8-DNP₆ (both without S9).

This data base will be invaluable for use by the ARB in their review of the PAH as potential toxic air contaminants. Furthermore, the magnitude of this data base allows a number of conclusions to be drawn concerning the similarities and differences between the sites. Thus, while the present study has provided only a "snapshot" of the ambient levels of PAH and PAH-derivatives and of ambient POM mutagenicity at each site, significant differences among the sampling locations were seen. Mammoth Lakes, the residential wood-burning impacted site, was characterized by high ambient PAH concentrations with only a small amount of atmospheric transformations; Concord had high PAH levels with a significant amount of atmospheric transformation products; Glendora had somewhat lesser ambient levels of the PAH with a higher fraction of atmospheric transformations; Oildale had low PAH concentrations and low atmospheric conversion, and Yuba City and Reseda were between Glendora and Oildale in terms of both ambient PAH concentrations and the degree of atmospheric transformations. As expected, Pt. Arguello and San Nicolas Island were characterized by low ambient levels of both the PAH and PAH-derivatives.

By examining relationships between the PAH, it is evident that the emission profiles of the various PAH depend on the individual sites

Table XI-1. PAH and PAH-Derivatives Identified and Quantified in Ambient Air During this Study

<u>PAH</u>	<u>S-Containing PAH</u>
Naphthalene	Dibenzothiophene
1-Methylnaphthalene	
2-Methylnaphthalene	<u>Nitroarenes</u>
Biphenyl	1-Nitronaphthalene
Acenaphthene	2-Nitronaphthalene
Acenaphthylene	3-Nitrobiphenyl
Fluorene	9-Nitroanthracene
Phenanthrene	2-Nitrofluoranthene
Anthracene	8-Nitrofluoranthene
Fluoranthene	1-Nitropyrene
Pyrene	2-Nitropyrene
Acephenanthrylene	7-Nitrobenz[a]anthracene
Benzo[ghi]fluoranthene	
Cyclopenta[cd]pyrene	
Benzo[c]phenanthrene	
Benzo[a]anthracene	
Chrysene	
Triphenylene	
Benzo[b]fluoranthene	
Benzo[j]fluoranthene	
Benzo[k]fluoranthene	
Benzo[a]pyrene	
Benzo[e]pyrene	
Anthanthrene	
Benzo[ghi]perylene	
Indeno[1,2,3-cd]fluoranthene	
Indeno[1,2,3-cd]pyrene	
Benzo[b]chrysene	
Benzo[c]chrysene	
Dibenz[a,c]anthracene	
Dibenz[a,h]anthracene	
Dibenz[a,j]anthracene	
Picene	
Coronone	
Retene	

sampled, and that a single simple PAH (such as naphthalene) cannot be used as a surrogate for the spectrum of PAH emitted into the atmosphere. The ambient air data also showed that retene (1-methyl-7-isopropylphenanthrene) is useful as a marker compound for coniferous wood burning. However, no marker compounds were evident for industrial or automotive emission sources.

Interestingly, the above observations concerning the ambient PAH burden and the degree of atmospheric transformation which had occurred between source and sampler at each site were mirrored by the ambient direct-acting mutagen densities measured. Thus, the average ambient mutagen densities at the seven sites leads to the ranking of: Concord > Glendora > Yuba City > Reseda > Oildale ~ Mammoth Lakes > Pt. Arguello. This finding, and the correlation between the direct-acting POM mutagen density and the 2-nitropyrene concentration (with 2-nitropyrene being formed in the atmosphere from the gas-phase OH radical reaction with pyrene), implies that the direct-acting mutagen density is associated with the particle-associated atmospheric reaction products of the primary emissions. If this conclusion is indeed correct, then the ambient POM mutagen density is an indicator of atmospheric transformation products, and can be used as a measure of the amount of reaction products present in ambient air in the particle phase.

This concept of the direct-acting mutagen density being associated with atmospheric transformation products has important implications for regulatory decisions concerning future PAH control strategies. Thus, although mutagenicity testing of specific individual emission sources may provide an indication of the relative source strengths, such testing is not a good measure of direct-acting mutagenicity at receptor sites because of atmospheric transformations which occur during transport to the receptor site.

Finally, the PAH and PAH-derivatives identified and quantified in this study, when combined with their direct-acting mutagenicities as measured in our laboratory, accounted for <10%, and generally <5%, of the measured direct-acting ambient POM mutagen densities. Thus, >90% of the mutagenicity was not accounted for and, consistent with the discussion above and in Section X, is probably associated with other PAH reaction products, and specifically with the more polar PAH atmospheric

transformation products. Such an expectation is totally consistent with laboratory studies of the OH radical-initiated reactions of the gas-phase PAH, which show that the nitroarenes account for <5%, and generally <1%, of the total reaction products, with the hydroxy- and hydroxynitro-PAH being about an order of magnitude more abundant.

We thus recommend that laboratory and ambient air studies be carried out to identify and quantify the products, in addition to the nitroarenes, formed from the atmospheric reactions of PAH and to determine the atmospheric concentrations of these species and their contribution to the direct-acting mutagenicity of ambient air (both volatile and particle-phase). Only through the identification and measurement of the chemical compounds responsible for the measured mutagenicity of ambient air can reliable risk assessments be carried out and the optimum control strategies be developed for the reduction of PAH and PAH-derivatives in ambient atmospheres.

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