A SURVEY OF AMBIENT CONCENTRATIONS OF SELECTED POLYCYCLIC AROMATIC HYDROCARBONS (PAH) AT VARIOUS LOCATIONS IN CALIFORNIA

Final Report

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ARB-88:pahsurvey

Abstract

Ambient air samples were collected during 1986-87 at seven sites throughout California impacted by different combustion emissions. The sites and the dominant combustion emissions were as follows: Glendora, vehicle emissions; Yuba City, agricultural burning; Concord, industrial emissions; Mammoth Lakes, wintertime residential wood burning; Oildale, oil production emissions; Reseda, chosen as a residential site; and Pt. Arguello, chosen as a background/rural site. At these sites, a total of 118 12-hr daytime and nighttime ambient air samples were collected onto Tenax-GC solid adsorbent, Teflon-impregnated glass fiber (TIGF) filters, and TIGF filters backed up by polyurethane foam (PUF) plugs. In addition, ambient particles were collected on TIGF filters at San Nicolas Island during the 1987 summertime South Coast Air Quality Study. These ambient air samples were subjected to chemical analysis for 32 polycyclic aromatic hydrocarbons (PAH), nine nitroarenes and one sulfur heterocycle and to mutagenicity testing on strains TA98 (with and without S9) and TA98NR and TA98/1,8-DNP_6 (both without S9) [the PUF plug and TIGF filter samples being composited into 24 and 25 samples, respectively, for the chemical analysis]. Large differences were observed among the sites for PAH and nitroarene concentrations and mutagenicity, with Concord having the highest PAH and nitroarene concentrations and mutagen densities, and Pt. Arguello the lowest. Among the PAH and PAH-derivatives monitored, 2-nitropyrene correlated the best with ambient mutagenicity (strain TA98, -S9). Since 2-nitropyrene is formed in the atmosphere from the gas-phase reaction of pyrene with the hydroxyl radical (in the presence of oxides of nitrogen), this suggests that the direct-acting mutagen densities of ambient particulate organic matter may be associated with atmospheric transformation products. The ambient concentrations of the PAH and PAH-derivatives measured during this program will provide one important element of the data base required by the California Air Resources Board for its review of the PAH as a potential toxic air contaminant.

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The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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GLOSSARY OF TERMS, ABBREVIATIONS AND SYMBOLS

Alkyl-PAH	Alkylated polycyclic aromatic hydrocarbons
ARB	Air Resources Board
Atm	Atmosphere (pressure)
Azaarenes	PAH containing a nitrogen atom
°C	Degrees Centigrade
CH_2Cl_2	Dichloromethane, methylene chloride
CH_3OH	Methanol
DMSO	Dimethyl sulfoxide
DOAS	Differential optical absorption spectroscopy
°F	Degrees Fahrenheit
EPA	U. S. Environmental Protection Agency
eV	Electron Volt
g	Gram
GC	Gas chromatography
GC/MS	Combined gas chromatography/mass spectrometry
GC/MS/MID	GC/MS operating in the multiple ion detection mode
GF	Glass fiber (filters)
Hetero-PAH	Polycyclic aromatic hydrocarbons containing a heteroatom (N, S or O)
Hg	Mercury
Hi-vol	High-volume sampler
HPLC	High performance liquid chromatography
L-broth or LB-broth	Growth medium for overnight culture of Salmonella strains
Lifetime	The time required for the reactant concentration to fall to 1/e of its initial value
m^3	Cubic meter
M	Molar
mg	Milligram
MID	Multiple ion detection
min	Minute
min^{-1}	Per minute
mL	Milliliter
mol	mole (6.022×10^{23} molecules)
MS	Mass spectrometry

GLOSSARY
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MSD	Mass selective detector
Mutagen density	Atmospheric mutagenicity "concentration"; total activity divided by sampling volume (rev m^{-3})
Mutagen loading	Specific mutagenicity of the particulate matter; total activity divided by particulate weight (rev mg^{-1})
M.W.	Molecular weight
m/z	Mass to charge ratio
$NADP^+$	Nicotinamide adenine dinucleotide phosphate; cofactor for S9 activation
NBS-SRM	Standard Reference Material supplied by the National Bureau of Standards
ng	Nanogram (10^{-9} gram)
nm	Nanometer
Nitroarene	PAH containing nitro (NO_2) group(s)
NO_3	Gaseous nitrate radical
NO_x	Oxides of nitrogen ($NO + NO_2$)
N_2O_4	Dinitrogen tetraoxide
N_2O_5	Dinitrogen pentoxide
O_3	Ozone
O.D.	Optical density
OH	Hydroxyl radical
Open column chromatography	Liquid chromatography technique, used for compound separation or purification
PAH	Polycyclic aromatic hydrocarbons
PASH	PAH containing a sulfur atom
PDT	Pacific daylight time
pg	Picogram (10^{-12} gram)
pH	$-\log_{10}[H]^+$; $[H]^+$ = hydrogen ion concentration in mol ℓ^{-1}
POM	Particulate organic matter, i.e., the organic extracts of the collected particles which are comprised of a spectrum of organic species, including PAH and PAH-derivatives.
ppb	Part per billion
ppt	Part per trillion
PST	Pacific standard time

GLOSSARY
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PUF	Polyurethane foam
rev	Revertants; net response above background in the Salmonella mutagenicity test
rpm	Revolutions per minute
S9	Supernatant from a 9000 x g centrifugation of rat liver homogenate
SAPRC	Statewide Air Pollution Research Center
SCAQS	South Coast Air Quality Study
SCFM	Standard cubic feet per minute
Semi-prep column	Semi-preparative scale column used for compound separation or purification by HPLC
Specific activity	Specific mutagenicity of the particulate extract; slope of the Salmonella dose-response curve (rev μg^{-1})
SRM 1647	NBS-SRM priority pollutant polynuclear aromatic hydrocarbons
SRM 1649	NBS-SRM Urban dust/organics
TA98	Ames Salmonella typhimurium strain, detects frameshift mutations. Most sensitive strain for detecting ambient particulate mutagens
TA98NR	Nitroreductase-deficient isolate of strain TA98; less sensitive than TA98 to many mononitroarenes
TA98/1,8-DNP_6	Transacetylase-deficient isolate of strain TA98; less sensitive than TA98 to dinitropyrenes
Tenax-GC	Adsorbent polymer of 2,6-diphenyl-p-phenylene oxide
TIC	Total ion chromatogram
TIGF	Teflon impregnated glass fiber (filters)
Torr	Pressure unit equivalent to 1 mm Hg
Total activity	The product of specific activity and total extract weight for a given collection period (rev)
TSP	Total suspended particulate
µg	Microgram (10^{-6} gram)
µℓ	Microliter (10^{-6} liter)
µm	Micrometer (10^{-6} meter)
µmol	Micromole (10^{-6} mole)
UV	Ultraviolet
uv/vis	Ultraviolet/visible
W	Watt

I. PROJECT SUMMARY

Polycyclic aromatic hydrocarbons (PAH) are emitted from combustion sources (Nikolaou et al. 1984), which include automobiles, industrial processes, domestic heating systems, waste incineration facilities, tobacco smoking and agricultural burns, as well as forest fires and volcanic eruptions. As a result of the ubiquitous presence of these combustion sources, PAH are distributed throughout the atmosphere in the gas and particulate phases. However, the proximity to emission sources, as well as meteorological factors, may result in markedly varying local concentrations. Many of the PAH compounds are animal carcinogens (NAS 1983), and a number of studies concerning the mechanisms of activation of PAH and the relationship between PAH mutagenicity and carcinogenicity have been carried out (see, for example, Burdette 1955 and Brookes 1977).

Because of the toxic nature of the PAH, hetero-PAH and their derivatives (including the nitroarenes), this general class of organic compounds is included on the California Air Resources Board's (ARB) list of potential toxic air contaminants, formulated in response to Assembly Bill 1807. Measurement of ambient atmospheric concentrations to which Californians are exposed is a critical element of the data base which must be assembled by the ARB and the Department of Health Services prior to their review and any regulatory actions on a potential toxic air contaminant. This requirement formed the basis for the present study to survey the ambient concentrations of selected PAH and PAH-derivatives at various locations in California.

Thus, the objectives of this program were to identify and quantify a series of PAH and PAH-derivatives (selected on the basis of their biological activities) present in ambient air at a number of locations in California which were representative of different combustion-generated emission sources. Ambient air sampling was carried out at locations which were impacted to a significant, or dominant, extent by the following emission sources: motor vehicle emissions, agricultural burning, residential wood burning, industrial emissions, emissions associated with oil-producing facilities. Additional sites were chosen to be representative of residential and rural areas. An important goal of this ambient air measurement program was to identify and quantify the volatile PAH and PAH-

derivatives as well as the particle-associated species. In addition to chemical analysis of PAH and PAH-derivatives, particulate matter was collected for mutagenicity testing using the Salmonella typhimurium bioassay.

The site heavily impacted by motor vehicle emissions was selected by the ARB to be at Citrus College, Glendora, at which the ARB-funded "Carbonaceous Species Methods Comparison Study" was conducted in August 1986. The locations of the remaining sites were as follows, in the order they were sampled:

Agricultural burning impacted site: Yuba City, sampled during October 1986.

Industrial emissions impacted site: Concord, sampled during December 1986 and January 1987.

Residential area impacted by wood burning emissions: Mammoth Lakes, sampled during February and March 1987.

Oil production impacted site: Oildale, sampled during March and April 1987.

Residential location: Reseda, sampled during May and June 1987.

Rural site: Pt. Arguello (Vandenberg Air Force Base), sampled during July 1987.

In addition, POM samples were collected at a "background" clean-air site, San Nicolas Island, during the intensive study days of the South Coast Air Quality Study (SCAQS) program during the June-September 1987 summertime sampling period. The locations of the sampling sites within California are shown in Figure I-1. Three different collection media, Tenax-GC solid adsorbent, polyurethane foam (PUF) plugs and Teflon-impregnated glass fiber (TIGF) filters, were employed for ambient air sampling at Glendora, Yuba City, Concord, Mammoth Lakes, Oildale, Reseda and Pt. Arguello. For the ambient air sampling carried out at San Nicolas Island, only TIGF filters were used to collect particulate matter.

From the sites in Glendora, Yuba City, Concord, Mammoth Lakes, Oildale, Reseda and Pt. Arguello, a total of 118 sets of ambient air samples were collected, with each sample set being of 12-hr daytime or

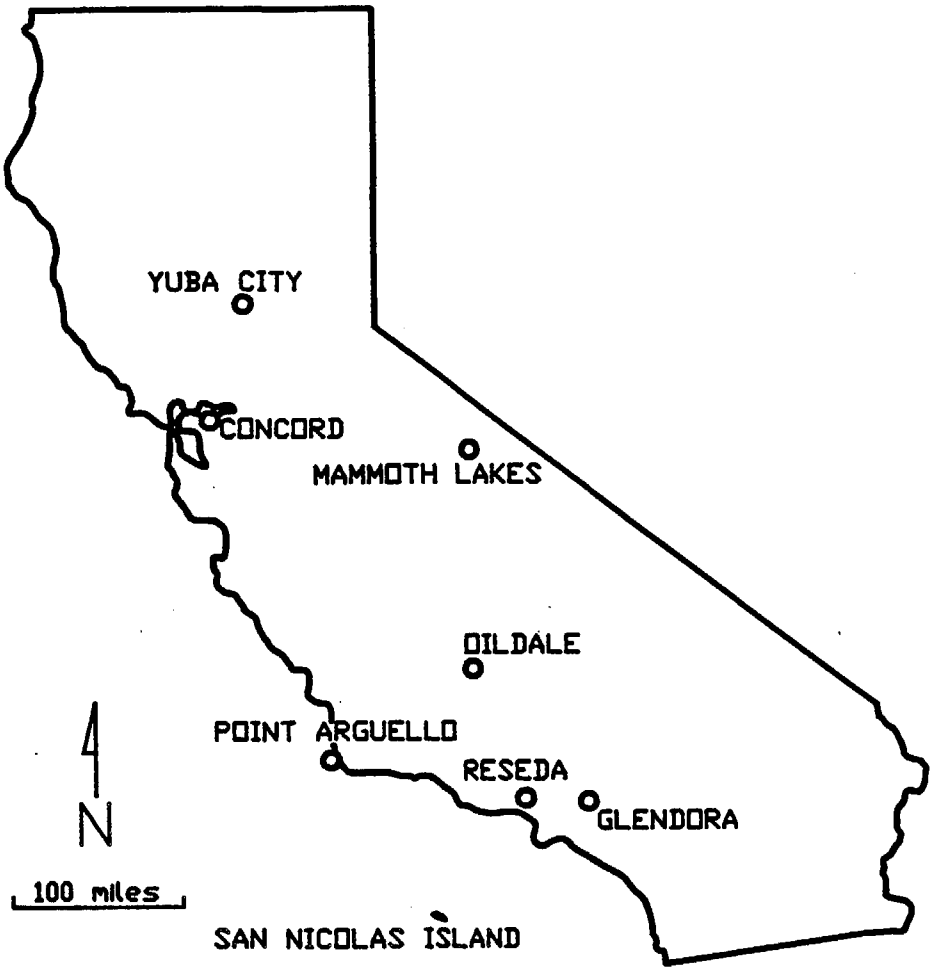

Figure I-1. Locations of the sites (O) at which ambient air sampling was carried out.

nighttime duration. Two of the TIGF filters from high-volume samplers equipped with inlets from each sample period were used for mutagenicity testing towards the following strains: TA98, -S9; TA98, +S9; TA98NR, -S9; and TA98/1,8-DNP_6, -S9. While the 118 ambient air samples collected on the Tenax solid adsorbent were each analyzed for naphthalene, the samples collected on the PUF plugs and filters were composited into 24 samples (plus a composited filter sample from San Nicolas Island) for chemical analysis. The analysis procedure for the PUF plugs and filters is described in detail in Section VI. The PAH and PAH-derivatives which were identified and quantified in this study are given in Table I-1. Including the mutagenicity testing and replicate chemical analyses, some 2500 individual data points were obtained.

The data obtained for the PAH and PAH-derivative concentrations, and for the ambient POM mutagenicity levels, are given in detail in Sections IV and VII, and average levels of selected parameters at the individual sites are given in Table I-2. Using the PAH and PAH-derivative ambient concentration data and the ambient levels of the direct-acting POM mutagen density, we conclude that:

- The emission profiles of the PAH differed from site to site, and no simple PAH can be used as a marker compound for the range of PAH observed in ambient air.
- Retene (1-methyl-7-isopropylphenanthrene) is a tracer for coniferous wood combustion.
- No obvious tracer compounds were observed for other specific combustion sources such as industrial emissions and emissions from automobiles.
- Significant differences in the ambient PAH concentrations and in the amounts of atmospheric transformations which had occurred between source and sampler were observed between different sites.
- The measured ambient particulate organic matter (POM) direct-acting mutagen densities correlate with the amounts of OH radical reaction products present in the atmospheres of the locations sampled. However, the contributions of the measured particle-associated PAH and PAH-derivatives to the direct-acting mutagen densities were <10%, and generally <5%, showing that the majority of this mutagenicity is presently not accounted for.

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

PAH	S-Containing PAH
Naphthalene	Dibenzothiophene
1-Methylnaphthalene	
2-Methylnaphthalene	Nitroarenes
Biphenyl	
Acenaphthene	1-Nitronaphthalene
Acenaphthylene	2-Nitronaphthalene
Fluorene	3-Nitrobiphenyl
Phenanthrene	9-Nitroanthracene
Anthracene	2-Nitrofluoranthene
Fluoranthene	8-Nitrofluoranthene
Pyrene	1-Nitropyrene
Acephenanthrylene	2-Nitropyrene
Benzo[ghi]fluoranthene	7-Nitrobenz[a]anthracene
Cyclopenta[cd]pyrene	
Benzo[c]phenanthrene	
Benz[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	

Table I-2. 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(cd)pyrene	Retene	2-NF[a]	1-NP[a]	2-NP[a]	Mutagenicity (TA98) -S9	+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	-		

[a]Benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), 2-nitrofluoranthene (2-NF), 1-nitropyrene (1-NP), 2-nitropyrene (2-NP).

We conclude that atmospheric transformations of the PAH present (at least partially) in the gas phase are highly important, leading to the formation of a spectrum of polar products, including nitroarenes, which contribute to the measured mutagen densities of ambient air. The occurrence of such atmospheric transformations must be taken into account in risk assessments and in the development of control strategies for the reduction of PAH and PAH-derivatives.

II. INTRODUCTION

A. Background

Polycyclic aromatic hydrocarbons (PAH) are formed in combustion systems at high temperatures (Bockhorn et al. 1982, Prado et al. 1985, Toqan et al. 1985, Kittelson et al. 1985), and hence are emitted from essentially all combustion sources. As discussed in the review of Nikolaou et al. (1984), these combustion sources include emissions from automobiles, industrial processes, domestic heating systems, waste incineration facilities, tobacco smoking, agricultural burns and several natural sources, including forest fires and volcanic eruptions. As a result of the ubiquitous presence of these combustion sources, PAH are distributed throughout the atmosphere in the gas and particulate phases. However, the proximity to emission sources, as well as meteorological factors, may result in markedly varying local concentrations.

Occupational hazards resulting from exposure to combustion-generated soot particles were indicated for the first time more than two centuries ago (Pott 1775), and several convincing proofs of the relationship between cancer and exposure to coal tars date back to the early part of this century (Yamagiwa and Ichikawa 1918). The first pioneering studies concerning the chemical composition of combustion-derived materials were conducted from the 1920's onward by Sir Ernest Kennaway and his colleagues (see the reviews by Kennaway 1955 and Phillips 1983), who identified the carcinogen benzo[a]pyrene as a constituent of these materials. The decade from 1933 to 1942 was one of intensive research into the synthesis and structure determination of PAH, during which thousands of such compounds were synthesized and several hundred tested for carcinogenicity (Shear and Leiter 1941, Badger et al. 1942). These studies have provided substantial evidence that many PAH compounds are animal carcinogens [see the U. S. National Academy of Sciences report (NAS 1983) for a list of these PAH]. Subsequently, studies concerning the mechanisms of activation of PAH and the relationship between PAH mutagenicity and carcinogenicity have been carried out (see, for example, Burdette 1955 and Brookes 1977).

A major breakthrough occurred in 1973, when Ames and co-workers (Ames et al. 1973a,b) described a short-term mutagenicity bioassay using a series of histidine-requiring Salmonella typhimurium strains which were

particularly sensitive to mutation by chemical carcinogens, thus allowing for a rapid screening of potentially hazardous compounds. Using these strains and a mammalian liver S9 activation system, Ames et al. (1973b) were able to demonstrate the mutagenicity towards Salmonella typhimurium of 18 carcinogens, including several PAH. More recently, it has been shown that extracts of respirable ambient particulate matter are strongly mutagenic in the Ames assay (see, for example, Pitts et al. 1977, Talcott and Wei 1977, Tokiwa et al. 1977, Pitts et al. 1982a). These extracts in general do not require microsomal activation for expression of their mutagenicity (and hence are "direct-acting") in contrast to the PAH which are mutagenic only in the presence of mammalian microsomal activation.

Although the chemical compounds responsible for the direct-acting mutagenicity of ambient POM have not yet been determined to any significant extent, nitrated PAH, many of which are strong direct-acting mutagens, have been shown to be constituents of ambient POM (Gibson 1983, Nielsen 1983, Tokiwa et al. 1983, Nielsen et al. 1984, Pitts et al. 1985a, Sweetman et al. 1986, Ramdahl et al. 1986, Arey et al. 1987), diesel (Schuetzle et al. 1981, 1982; Pitts et al. 1982b, Xu et al. 1981, 1982) and gasoline (Gibson 1982, 1983) exhaust particulates, soot from wood-burning fireplaces (Gibson 1982, 1983; Nishioka et al. 1982) and coal fly ash (Hanson et al. 1983, Harris et al. 1984). Interest in these nitroarenes has been heightened by the recent observation of the induction of rat mammary gland tumors by 1-nitropyrene (Hirose et al. 1984) and the induction of sarcomas in rats by subcutaneous injection of dinitropyrenes (Ohgaki et al. 1984, 1985). Evaluations of the health effects of the nitropyrenes and mechanistic studies of their carcinogenicities continue (see, for example, Djuric et al. 1988 and King 1988).

While a variety of nitroarenes are present, together with the PAH, in emissions from combustion sources, it is now clear that the majority of the mononitroarenes observed in ambient atmospheric particulate matter are formed from their parent PAH during transport through the atmosphere from source to receptor (Pitts et al. 1985a, Ramdahl et al. 1986). Thus, in order to assess the exposure of human populations to airborne toxic chemicals, it is necessary to measure the ambient atmospheric concentrations of PAH, their nitroderivatives, and other PAH-derivatives, and to

determine the chemical processes leading to the formation of these PAH-derivatives in the atmosphere.

In addition to the PAH and nitroarenes, sulfur- and nitrogen-containing heterocyclic analogues of PAH have been shown to occur in numerous sources, such as coal-derived products, shale-oil (Lee et al. 1980, Willey et al. 1981, Nishioka et al. 1986) and synthetic fuels (Radian Corp. 1977, Ho et al. 1980). Although the biological activities of these hetero-PAH compounds are not well known, research indicates that they may contribute to the mutagenic and/or carcinogenic activity of synthetic fuels (Guerin et al. 1980, Ho et al. 1981, Karcher et al. 1981, Pelroy et al. 1983, McFall et al. 1984).

Because of the toxic nature of the PAH, hetero-PAH and their derivatives (including the nitroarenes), this general class of organic compounds is included on the California Air Resources Board's (ARB) list of potential toxic air contaminants, formulated in response to Assembly Bill 1807. Measurement of ambient atmospheric concentrations to which Californians are exposed is a critical element of the data base which must be assembled by the ARB and the Department of Health Services prior to their review and final regulatory actions on a potential toxic air contaminant. This requirement forms the basis for the present study to survey the ambient concentrations of selected PAH and PAH-derivatives at various locations in California.

B. Objectives

The objectives of this program were to identify and quantify a series of PAH and PAH-derivatives (selected on the basis of their biological activities) present in ambient air at a variety of locations in California which were representative of different combustion-generated emission sources. Ambient air sampling was carried out at locations which were impacted to a significant, or dominant, extent by the following emission sources: motor vehicle emissions, agricultural burning, residential wood burning, industrial emissions, emissions associated with oil-producing facilities. Additional sites were chosen to be representative of residential and rural areas. An important feature of this ambient air measurement program was the goal of sampling for, and identifying and quantifying, the volatile PAH and PAH-derivatives as well as the particle-associated species. In addition to the identification and quantification

of PAH and PAH-derivatives, POM samples were collected for mutagenicity testing using the Salmonella typhimurium bioassay.

The data obtained from this experimental program provide the ARB with the ambient levels of PAH and PAH-derivatives to which Californians are exposed, and thus provide a data base for use by the California Air Resources Board in their review of the PAH and PAH-derivatives as potential toxic air contaminants.

C. Biological Activities of PAH and Lists of PAH Targeted for Monitoring

The carcinogenic and mutagenic activities of atmospherically relevant PAH, alkyl-PAH, N- and S-hetero-PAH and nitroarenes are summarized in Tables II-1 through II-4, respectively, together with their reported occurrence in ambient air (prior to this study) and primary emissions. These tables were compiled mainly from the review articles of Jacob et al. (1984, 1986), which dealt with 48 polycyclic pollutants of environmental and occupational interest which are available as certified high-purity reference materials from the Community Bureau of Reference (BCR). The availability of standard reference compounds was critical to the consideration of PAH and PAH-derivatives for selection for analysis in this study. The reviews by Jacob et al. (1984, 1986) superseded the earlier reviews published by the International Agency for Research on Cancer (IARC). Other recent reviews were used to develop Tables II-1 through II-4 and, where possible, are given as the references in these tables rather than single-source articles. For convenience these references are listed after Table II-4.

In evaluating carcinogenic activity, the notation of Jacob et al. (1984, 1986) has been used, as follows: -, inactive; (+), very weak; +, weak; ++, moderate; +++, strong; ++++, very strong. In some cases two evaluations are given, and these most often reflect conflicting determinations of carcinogenic activity (e.g., +/-). Other reviewers have used a different notation and, where necessary, original evaluations have been adjusted to correspond to the notation used by Jacob et al. (1984, 1986), where benzo[a]pyrene is evaluated as ++++. Compounds for which sufficient evidence of carcinogenicity has been found by IARC are noted, although the number of compounds evaluated by IARC was limited.

Table II-1. Polycyclic Aromatic Hydrocarbons

Compound Name	CAS Registry No.	M.W.	Carcinogenicity	Ref.	Mutagenicity	Ref.	Present in Ambient Air?	Ref.	Present in Emissions?	Ref.
Fluoranthene	206-44-0	202	-/+	6,13	-/+	6	+	6	+	13
Pyrene	129-00-0	202	-	6	-	6	+	6	+	6
Benzo[ghi]fluoranthene	203-12-3	226	-	6			+	6	+	6
Cyclopenta[cd]pyrene	27208-37-3	226	+/++	6	+++[a]	6	+	6	+	6
Benz[a]anthracene	56-55-3	228	+[b]	7	+/++[a]	7	+	7	+	7
Benzo[c]phenanthrene	195-19-7	228	++	6	++	6	+	6	+	6
Chrysene	218-01-9	228	+	7	++	7	+	7	+	7
Triphenylene	217-59-4	228	-/+	7	++	7	+	7	+	7
Benzo[b]fluoranthene	205-99-2	252	++/+++[b]	6	++	6	+	6	+	6
Benzo[j]fluoranthene	205-82-3	252	++/+++[b]	6	++/+++	6	+	6	+	6
Benzo[k]fluoranthene	207-08-9	252	+[b]	6	++	6	+	6	+	6
Benzo[a]pyrene	50-32-8	252	++++[b]	6	++++[a]	6	+	6	+	6
Benzo[e]pyrene	192-97-2	252	-/+	6,13	+	6	+	6	+	6
Anthanthrene	191-26-4	276	+/++	6	+	6	+	6	+	6
Benzo[ghi]perylene	191-24-2	276	-/+	6	+	6	+	6	+	6
Indeno[1,2,3-cd]fluoranthene	193-43-1	276	c	7	+	7	+	5	+	7
Indeno[1,2,3-cd]pyrene	193-39-5	276	++[b]	6	++	6	+	6	+	6
Benzo[b]chrysene	214-17-5	278	-	6	(+)	8	+	13		
Benzo[c]chrysene	194-69-4	278	++	6	+	8				
Benzo[g]chrysene	196-78-1	278	++	13						
Dibenz[a,c]anthracene (Benzo[b]triphenylene)	215-58-7	278	-/+	6	+++[a]	6	+	13		
Dibenz[a,h]anthracene	53-07-3	278	+++/++++[b]	6	++/+++[a]	6	+	6	+	6

(continued)

Table II-1 (continued) - 2

Compound Name	CAS Registry No.	M.W.	Carcinogenicity	Ref.	Mutagenicity	Ref.	Present in Ambient Air?	Ref.	Present in Emissions?	Ref.
Dibenz[a,j]anthracene	224-41-9	278	++	6	+	6	c	11		
Picene	213-46-7	278	+	7	+	7	+	1	+	7
Coronene	191-07-1	300	-/+	7,13	-/+	7	+	7	+	7
Benzo[rst]pentaphene (Dibenzo[a,i]pyrene)	189-55-9	302	+++/++++[b]	7	++	7	d	11	+	7
Dibenz[a,e]aceanthrylene (Dibenzo[a,e]fluoranthene)	5385-75-1	302	++	7	+++	7				
Dibenzo[a,e]pyrene	192-65-4	302	++/+++[b]	6	++	6	d	11	+	6
Dibenzo[a,h]pyrene	189-64-0	302	++++[b]	6	++++	6	+	6		
Dibenzo[a,l]pyrene	191-30-0	302	+++[b]	6			d	11		

[a]Sufficient evidence of activity in short-term tests (IARC Monographs, Vol. 32, December 1983).
[b]Sufficient evidence of carcinogenicity (IARC Monographs, Vol. 32, December 1983).
[c]Has not been tested.
[d]Four isomers of dibenzopyrene identified, but not specified.

Table II-2. Alkylpolycyclic Aromatic Hydrocarbons

Compound Name	CAS Registry No.	M.W.	Carcinogenicity	Ref.	Mutagenicity	Ref.	Present in Ambient Air?	Ref.	Present in Emissions?	Ref.
1-Methylphenanthrene	832-69-9	192	-	13	+[a]	13	+	11	+	13
1,4-Dimethylphenanthrene	22349-59-3	206	b	9	+	10	c	5	c	16
4,10-Dimethylphenanthrene	23189-63-1	206	b	9	+	10	c	5	c	16
2-Methylfluoranthene	33543-31-6	216	+	16	+	10	+	5	d	13
1,2,4-Trimethylphenanthrene	23189-64-2	220	+	3			e	5	e	16
1-Methylbenz[a]anthracene	2498-77-3	242	+/-	3	+	12	d	5	f	16
3-Methylbenz[a]anthracene	2498-75-1	242	+/-	3	+	12	d	5	f	16
4-Methylbenz[a]anthracene	316-49-4	242	+/-	3	+	12	d	5	f	16
5-Methylbenz[a]anthracene	2319-96-2	242	++	3	+	12	d	5	f	16
6-Methylbenz[a]anthracene	316-14-3	242	+++	3	+	12	d	5	f	16
7-Methylbenz[a]anthracene	2541-69-7	242	+++	3	++	12	d	5	f	16
8-Methylbenz[a]anthracene	2381-31-9	242	+++	3	+	12	d	5	f	16
9-Methylbenz[a]anthracene	2381-16-0	242	+/-	3	+	12	d	5	f	16
10-Methylbenz[a]anthracene	2381-15-9	242	+/-	3	+	12	d	5	f	16
11-Methylbenz[a]anthracene	6111-78-0	242	+/-	3	+	12	d	5	f	16
12-Methylbenz[a]anthracene	2422-79-9	242	+++	3	+	12	d	5	f	16
2-Methylbenzo[c]phenanthrene	2606-85-1	242	+	3			d	5		
3-Methylbenzo[c]phenanthrene	2381-19-3	242	+/-	3			d	5		
4-Methylbenzo[c]phenanthrene	4076-40-8	242	+/-	3			d	5		
5-Methylbenzo[c]phenanthrene	652-04-0	242	++	3			d	5		
6-Methylbenzo[c]phenanthrene	2381-34-2	242	++	3			d	5		
1-Methylchrysene	3351-28-8	242	-	6	+	6	+	5		
2-Methylchrysene	3351-32-4	242	+	6	+	6	+	5	+	6

(continued)

Table II-2 (continued) - 2

Compound Name	CAS Registry No.	M.W.	Carcinogenicity	Ref.	Mutagenicity	Ref.	Present in Ambient Air?	Ref.	Present in Emissions?	Ref.
3-Methylchrysene	3351-31-3	242	+	6	+	6	+	5	+	6
4-Methylchrysene	3351-30-2	242	+	6	+	6	d	11	+	6
5-Methylchrysene	3697-24-3	242	+++[g]	6	++/+++	6	d	11	+	6
6-Methylchrysene	1705-85-7	242	+	6	+	6	+	11	+	6
2-Methylbenzo[a]pyrene	16757-82-7	266	+++	3	+++	2	d	13		
3-Methylbenzo[a]pyrene	16757-81-6	266	+++	3	+	2	d	13		
4-Methylbenzo[a]pyrene	16757-83-8	266	+++	3	++++	2	d	13		
5-Methylbenzo[a]pyrene	31647-36-6	266	++	3	+	2	d	13		
6-Methylbenzo[a]pyrene	2381-39-7	266	+++	3	++++	2	d	13		
7-Methylbenzo[a]pyrene	63041-77-0	266	++	3	+	2	d	13		
11-Methylbenzo[a]pyrene	16757-80-5	266	+++	3	++++	2	d	13		
12-Methylbenzo[a]pyrene	4514-19-6	266	+++	3	+	2	d	13		
3-Methylcholanthrene	56-49-5	268	+++	3	++	12	+	5		
7-Methyldibenz[a,c]anthracene		292	++	3			d	13		
2-Methyldibenz[a,h]anthracene	63041-83-8	292	+	3			d	5		
3-Methyldibenz[a,h]anthracene	63041-84-9	292	+	3			d	5		
6-Methyldibenz[a,h]anthracene	63041-85-0	292	++	3			d	5		
7-Methyldibenz[a,h]anthracene	15595-02-5	292	+++	3			d	5		

[a]Sufficient evidence of activity in short-term tests (IARC Monographs, Vol. 32, December 1983).
[b]Tumorogenic, but not tested for complete carcinogenicity.
[c]Isomer unspecified. Could be dimethylanthracenes.
[d]Isomer unspecified.
[e]Isomer unspecified. Could be trimethylanthracenes.
[f]Isomers unspecified. Could be methylchrysenes.
[g]Sufficient evidence of carcinogenicity (IARC Monographs, Vol. 32, December 1983).

Table II-3. N- And S-Hetero Polycyclic Aromatic Hydrocarbons

Compound Name	CAS Registry No.	M.W.	Carcinogenicity	Ref.	Mutagenicity	Ref.	Present in Ambient Air?	Ref.	Present in Emissions?	Ref.
Quinoline	91-22-5	129	++	13	+	4	+	13		
Phenanthridine	229-87-8	179	++	13	+	4	+	13		
11H-Benzo[a]carbazole	13375-54-7	217	+	3	+	8	+	1		
Benz[a]acridine	225-11-6	229	-	6	+	8	+	6	+	6
Benz[c]acridine	225-51-4	229	+	6	+	6	+	6	+	6
Naphtho[2,3-f]quinoline (4-Azabenz[a]anthracene)	224-98-6	229	+	13			a	1		
Benzo[b]naphtho[1,2-d]thiophene	205-43-6	234	-	6	+	6	b	11		
Benzo[b]naphtho[2,1-d]thiophene	239-35-0	234	-	13	+	6	b	11		
10-Azabenzo[a]pyrene (Phenaleno[1,9-gh]quinoline)	189-92-4	253	+	6	+	6	c	1		
7H-Dibenzo[a,g]carbazole	207-84-1	267	+	3						
13H-Dibenzo[a,i]carbazole	239-64-5	267	+	3						
7H-Dibenzo[c,g]carbazole	194-59-2	267	++/+++[d]	7	-/(+)	7				
Benzo[h]naphtho[1,2-f]quinoline	196-79-2	279	++	3						
Dibenz[a,h]acridine	226-36-8	279	+[d]	3	+	8	+	6	+	6
Dibenz[a,j]acridine	224-42-0	279	+[d]	6	++	6	+	6	+	6
Dibenz[c,h]acridine	224-53-3	279	+	6	+	8				

[a]Four isomers of azabenz[a]anthracene identified, but unspecified.
[b]Three isomers of naphthobenzothiophene identified, but unspecified.
[c]Isomer unspecified.
[d]Sufficient evidence of carcinogenicity (IARC Monographs, Vol. 32, December 1983).

Table II-4. Nitropolycyclic Aromatic Hydrocarbons

Compound Name	CAS Registry No.	M.W.	Carcinogenicity	Ref.	Mutagenicity	Ref.	Present in Ambient Air?	Ref.	Present in Emissions?	Ref.
2-Nitronaphthalene	581-89-5	173	+	17	+	17				
5-Nitroacenaphthene	10353-99-8	199	+	17	+	17	+	13		
4-Nitrobiphenyl	92-93-3	199	+	17	++	17			+	17
2-Nitrofluorene	607-57-8	211	+	17	+++	17			+	17
3-Nitrofluoranthene	892-21-7	247	+	17	+++++[a]	17	+	15	+	17
1-Nitropyrene	5522-43-0	247	-/+	6	++++[a]	6	+	6	+	6
4-Nitropyrene	57835-92-4	247	+++	18						
2,7-Dinitrofluorene	5405-53-8	256	+	17	++++	17			+	17
7-Nitrobenz[a]anthracene	20268-51-3	273	+	18						
6-Nitrochrysene	7496-02-8	273	+++	17	+++	17				
1,3-Dinitropyrene	75321-20-9	292	+	17	+++++	17			+	17
1,6-Dinitropyrene	42397-64-8	292	++	18	+++++	17			+	17
1,8-Dinitropyrene	42397-65-9	292	++++	17	+++++[a]	17			+	17
6-Nitrobenzo[a]pyrene	63041-90-7	297	+	17	++++	14	+	13	+	17
3-Nitroperylene	20589-63-3	297	+	17	++	17				

[a]Sufficient evidence of activity in short-term tests (IARC Monographs, Vol. 32, December 1983).

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The notation used to evaluate mutagenic activity is the same as that used to evaluate carcinogenic activity, with the exception that the notation +++++ (highly active) has been given to certain nitroarenes which exhibit very much greater mutagenic activity in Salmonella than does benzo[a]pyrene [which is ++++ in the notation of Jacob et al. (1984, 1986)]. Although a large number of nitroarenes have been found to be mutagenic in Salmonella, the listings in Table II-4 have been restricted to those compounds which have been evaluated as carcinogenic in animal tests.

A number of carcinogenic and/or mutagenic PAH and PAH-derivatives have been excluded from Tables II-1 through II-4 because they have not been identified in ambient air or primary emissions, although they may have been identified in tobacco smoke condensates. While tobacco smoke is an important indoor air pollutant, it is not considered here to be relevant to the analysis of ambient air.

As noted in the tables, many compounds have been detected in ambient air or in combustion emissions based upon their gas chromatographic retention times and mass spectral parent ion, and thus the specific isomer has not been identified. This is especially true of methyl-substituted PAH, many isomers of which have been tested for carcinogenicity because of their usefulness as probes for understanding the mechanisms of activation of the parent hydrocarbon, but which are difficult to identify in environmental samples.

Based upon their expected concentrations in ambient air and in emissions from combustion sources (see above), together with their biological activities, the following lists (Tables II-5 through II-8) of PAH and PAH-derivatives were recommended for qualitative and/or quantitative analysis in the samples collected at the seven sites in California in this study. The sources of the PAH standards used in this study for retention time and mass spectral matching are also included in these tables. The structures of the PAH are given in Appendix A (adapted from Lee et al. 1981) which includes all the isomers of a given molecular weight, with those quantified and/or recommended for monitoring being starred.

Although the first four PAH listed in Table II-5 are neither carcinogenic nor mutagenic, they were recommended for quantification because their concentrations in emissions from various combustion sources are high. In addition, we have laboratory evidence which suggests that naphthalene, pyrene and fluoranthene may be transformed in the atmosphere to form toxic nitro-derivatives (see Section IX). The remaining PAH are as listed in Table II-1 above. Each of these PAH shows carcinogenic and/or mutagenic activity.

Due to the large number of isomeric PAH (there are, for example, seven PAH of M.W. 278 on our list), it was expected that isomer-specific identification and quantification would not always be possible. GC/MS analysis of the PAH-containing HPLC fraction of each sample was carried out using MID, with the monitored ions being the molecular ions listed in Table II-5 below. In this way we screened for the presence of all the PAH isomers of a given molecular weight, and isomer identification (and quantification) depended upon achieving the requisite gas-chromatographic resolution and on the availability of authentic standards for retention time matching.

Since only one or two of the several isomers of M.W. 206, 216 and 220 are listed in Table II-2 and have been reported to be biologically active, we did not analyze for these alkyl-PAH isomer groups. Instead, we have included the alkylated naphthalenes in Table II-6, since these PAH were expected to be present in ambient air in high concentrations. Due to the very large number of isomeric alkyl-PAH of M.W. 156, 192, 242, 266 and 292, and the very limited number of standards available, isomer-specific identification and quantification of these compounds were not possible. However, retene (1-methyl-7-isopropylphenanthrene) was quantified since this alkyl-PAH has been shown to be a specific marker for coniferous wood combustion (Ramdahl 1983).

The identification and quantification of most of the N- and S-hetero-PAH expected to be present in ambient POM was not possible due to the unavailability of standards for these PAH-derivatives (Table II-7). As potential markers for sources producing high quantities of N- and S-hetero-PAH, we originally had hoped to quantify quinoline (also shown to be carcinogenic, Table II-3), isoquinoline [identified in the urban dust

NBS SRM 1649 (Wise et al. 1982)] and dibenzothiophene [shown to be present in industrial, diesel and coal combustion emissions (Lee et al. 1977, Ciccioli et al. 1986)]. However, as discussed in Section VI, the analysis of nitrogen-containing PAH posed problems which were not totally resolved during this program and only dibenzothiophene was routinely identified and quantified at all sites during this study.

In addition to the nitroarenes listed in Table II-4, we included for quantification 2-nitrofluoranthene, 1-nitronaphthalene and 3-nitrobiphenyl, since we expected these nitroarenes to be present in ambient samples in relatively high concentrations. Similarly, we quantified the abundant and biologically-active nitroarenes 2-nitronaphthalene, 8-nitrofluoranthene and 1- and 2-nitropyrene. GC/MS with MID was used to screen for, and to identify and quantify whenever possible, the remaining nitroarenes listed below in each sample.

Additional species not on the above lists to be monitored which were quantified either because they were abundant or readily identified were: biphenyl, acenaphthylene, acenaphthene, fluorene, acephenanthrylene, perylene and 9-nitroanthracene.

Table II-5. PAH Recommended for Monitoring

	Compound	Molecular Weight	Source
1.	Naphthalene	128	Aldrich; NBS SRM 1647
2.	Anthracene	178	Aldrich; NBS SRM 1647
3.	Phenanthrene	178	Aldrich; NBS SRM 1647
4.	Pyrene	202	Aldrich; NBS SRM 1647
5.	Fluoranthene	202	Aldrich; NBS SRM 1647
6.	Benzo[ghi]fluoranthene	226	a
7.	Cyclopenta[cd]pyrene	226	b
8.	Benz[a]anthracene	228	Eastman; NBS SRM 1647
9.	Benzo[c]phenanthrene	228	a
10.	Chrysene	228	Aldrich; NBS SRM 1647
11.	Triphenylene	228	Aldrich
12.	Benzo[b]fluoranthene	252	NBS SRM 1647
13.	Benzo[j]fluoranthene	252	b
14.	Benzo[k]fluoranthene	252	NBS SRM 1647
15.	Benzo[a]pyrene	252	Aldrich; NBS SRM 1647
16.	Benzo[e]pyrene	252	Aldrich
17.	Anthanthrene	276	a
18.	Benzo[ghi]perylene	276	Aldrich; NBS SRM 1647
19.	Indeno[1,2,3-cd]fluoranthene	276	b
20.	Indeno[1,2,3-cd]pyrene	276	NBS SRM 1647
21.	Benzo[b]chrysene	278	a
22.	Benzo[c]chrysene	278	a
23.	Benzo[g]chrysene	278	Not available
24.	Dibenz[a,c]anthracene	278	Aldrich
25.	Dibenz[a,h]anthracene	278	NBS SRM 1647
26.	Dibenz[a,j]anthracene	278	a
27.	Picene	278	b
28.	Coronene	300	Aldrich
29.	Benzo[rst]pentaphene (Dibenzo[a,i]pyrene)	302	b

(continued)

Table II-5 (continued) - 2

	Compound	Molecular Weight	Source
30.	Dibenz[a,e]aceanthrylene	302	Not available
31.	Dibenzo[a,e]pyrene	302	a
32.	Dibenzo[a,h]pyrene	302	Aldrich
33.	Dibenzo[a,l]pyrene	302	a

[a]Obtained from Commission of the European Communities, Community Bureau of Reference, Brussels, Belgium.
[b]Obtained from Dr. W. Schmidt, Sieker Landstrasse 19, 2070 Ahrensburg, West Germany.

Table II-6. Alkyl-PAH Recommended for Monitoring

	Compound	Molecular Weight	Source
1.	1-Methylnaphthalene	142	Chem. Services
2.	2-Methylnaphthalene	142	Chem. Services
3.	Isomeric dimethylnaphthalenes	156	2,3-Dimethyl; Aldrich
4.	Isomeric methylanthracenes and methylphenanthrenes	192	2-, 9-Methylanthracene; Aldrich
5.	Isomeric methylbenzanthracenes, methylbenzophenanthrenes and methylchrysenes	242	Not available
6.	Isomeric methylbenzo(a)pyrenes	266	Not available
7.	Isomeric methyldibenzanthracenes	292	Not available
8.	Retene	234	ICN-KOR Isotopes

Table II-7. N- and S-Containing Hetero-PAH Recommended for Monitoring

	Compound	Molecular Weight	Source
1.	Quinoline	129	Alfa
2.	Isoquinoline	129	Aldrich
3.	Isomers: phenanthridine, acridine, benzoquinolines and benzoisoquinolines	179	Phenanthridine, acridine; Aldrich
4.	Benzocarbazoles	217	Not available
5.	N-hetero-PAH (29 isomers) including benz[a]acridine, benz[c]acridine and naphtho[2,3-f]quinoline	229	Benz[c]acridine[a]
6.	Isomeric dibenzocarbazoles	267	Not available
7.	Isomeric dibenzacridines	279	Not available
8.	Dibenzothiophene	184	Aldrich
9.	Isomeric methyldibenzothiophenes	198	Not available
10.	Isomeric benzonaphthothiophenes	234	Not available

[a]Gift from Dr. Victor Snieckus, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

Table II-8. Nitro-PAH Recommended for Monitoring

	Compound	Molecular Weight	Source
1.	1-Nitronaphthalene	173	Aldrich
2.	2-Nitronaphthalene	173	Aldrich
3.	5-Nitroacenaphthene	199	a
4.	3-Nitrobiphenyl	199	Aldrich
5.	4-Nitrobiphenyl	199	Aldrich
6.	2-Nitrofluorene	211	Aldrich
7.	1-,3-,7- and 8-Nitrofluoranthenes	247	a
8.	2-Nitrofluoranthene	247	a
9.	1-Nitropyrene	247	Pfaltz and Bauer[b]
10.	2-Nitropyrene	247	c
11.	4-Nitropyrene	247	d
12.	2,7-Dinitrofluorene	256	Aldrich
13.	Isomeric Nitrobenz[a]anthracenes	273	7-Nitro[a]
14.	6-Nitrochrysene	273	Analabs
15.	1,3-, 1,6- and 1,8-Dinitropyrenes	292	a
16.	6-Nitrobenzo[a]pyrene	297	a
17.	3-Nitroperylene	297	a

[a]Synthesized; see Section VI-D for details.
[b]Purified according to the method described by Paputa-Peck et al. (1983).
[c]Gift from Dr. D. Schuetzle, Ford Motor Co., Dearborn, MI.
[d]Gift from Dr. A. Berg, University of Aarhus, Denmark.

III. SAMPLING SITES AND AMBIENT AIR SAMPLING PROCEDURES

A. Sampling Sites

As noted in Section II above, the objectives of this program were to monitor the ambient concentrations of PAH and PAH-derivatives at several locations in California impacted by differing combustion emission sources. As stated in the ARB's Request for Proposal, measurements were carried out at seven locations characterized as being:

(a) Residential
(b) Rural
(c) Industrial
(d) Agricultural burn
(e) Populated mountain area during the peak of the wood-burning season
(f) Oil production
(g) Motor vehicle impacted

The sampling location designated as (g), a site heavily impacted by motor vehicle emissions, was selected by the ARB to be at Citrus College, Glendora, at which the ARB-funded "Carbonaceous Species Methods Comparison Study" was conducted in August 1986.

The locations of the remaining sites were arrived at after extensive discussions with the ARB staff, and were as follows, in the order they were sampled:

Agricultural burning impacted site: Yuba City, sampled during October 1986.

Industrial emissions impacted site: Concord, sampled during December 1986 and January 1987.

Residential area impacted by wood burning emissions: Mammoth Lakes, sampled during February and March 1987.

Oil production impacted site: Oildale, sampled during March and April 1987.

Residential location: Reseda, sampled during May and June 1987.

Rural site: Pt. Arguello (Vandenberg Air Force Base), sampled during July 1987.

In addition, at the request of the ARB we arranged to have POM samples collected at a "background" clean-air site, San Nicolas Island, during the intensive study days of the South Coast Air Quality Study (SCAQS) program during the June-September 1987 summertime sampling period.

The overall schedule for this program was designed to allow sampling to be carried out at approximately two-month intervals, with the time at any one site being approximately two to four weeks. The goal was to sample for approximately seven to ten days at a given site, with the time of year chosen to maximize the pollutant levels at certain of these locations (for example, at Yuba City, Concord and Mammoth Lakes). Thus, at Yuba City and Mammoth Lakes, sampling was conducted during days when agricultural burns (Yuba City) or wood burning (Mammoth Lakes) was occurring. Similarly, at Concord, sampling was carried out under meteorological conditions conducive to high pollutant levels (light winds from the north or northwest). At the sites in Oildale, Reseda and Pt. Arguello, sampling was carried out for one or two prolonged periods since reasonably constant meteorological conditions prevailed during these sampling periods.

The locations of the sampling sites within California are shown in Figure III-1, and more detailed maps showing the locations of the sites at Glendora, Yuba City, Concord, Mammoth Lakes, Oildale, Reseda and Pt. Arguello are shown in Figures III-2 through III-8, respectively. The locations of the sampling sites are described in more detail below.

Glendora. The site of the ARB-funded "Carbonaceous Species Methods Comparison Study" was on the campus of Citrus College (Figure III-2), with sampling carried out adjacent to the football stadium. The samplers were positioned just north of the trailers and mobile vans of the other investigators.

Yuba City. Ambient air sampling was carried out on the grounds of the local Air Pollution Control District monitoring station (Figure III-3).

Concord. After much effort to locate a sampling site which would be downwind of the industrial complexes in the Concord/Martinez area, a sampling site at the Bollman Water Treatment Plant in Concord (Figure III-4) was finally chosen.

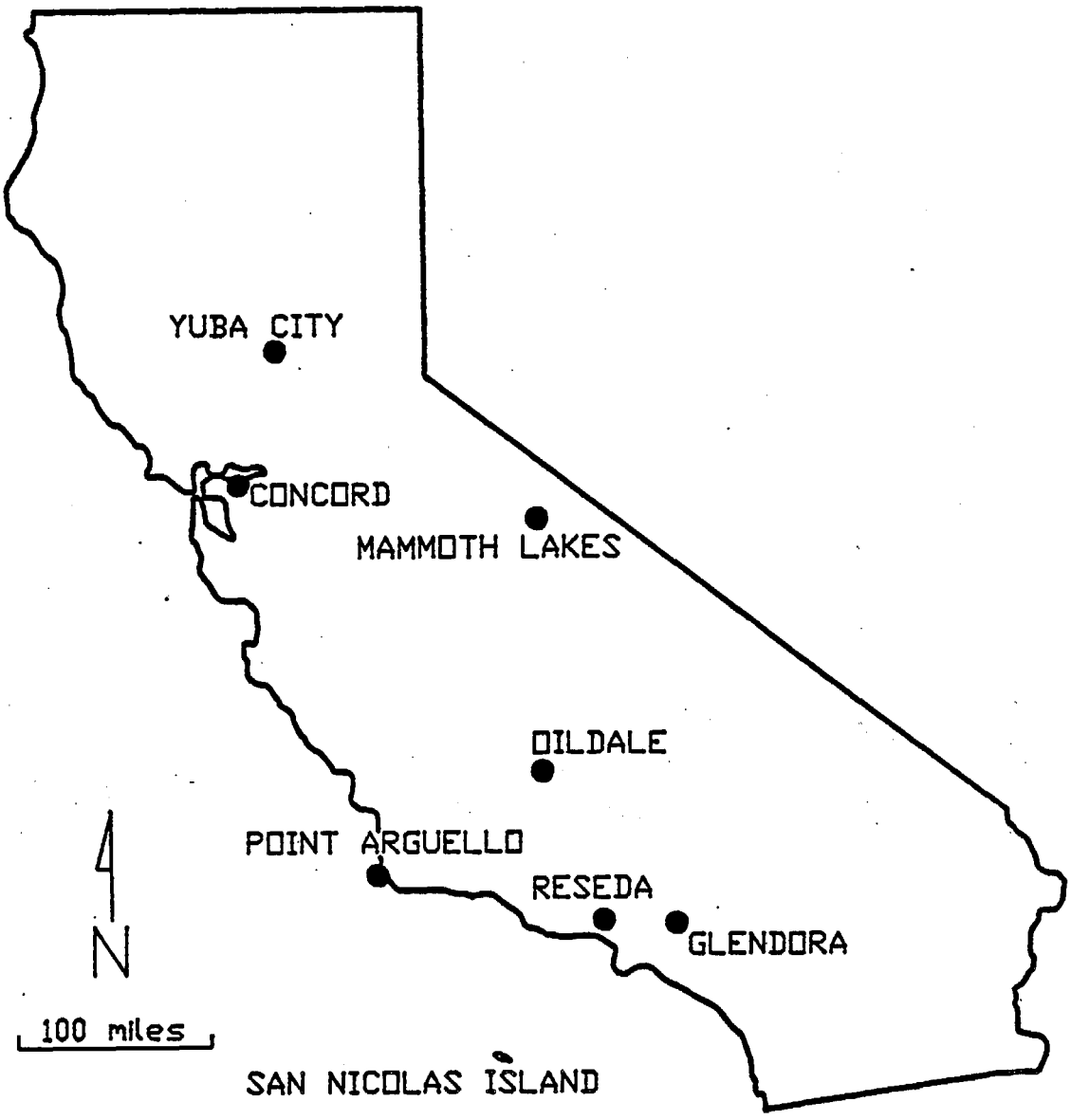


Figure III-1. Locations of the sites (●) at which ambient air sampling was carried out.

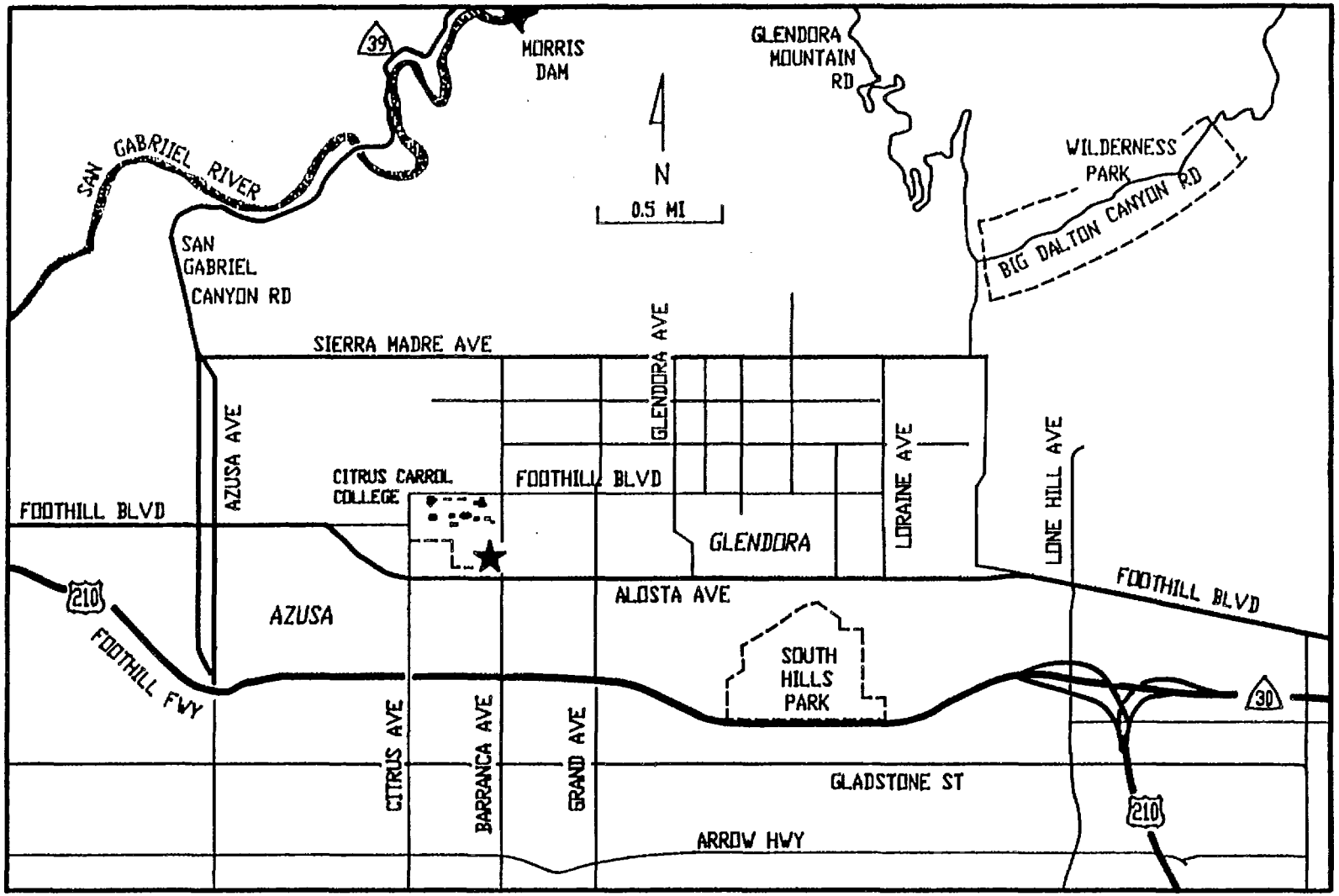


Figure III-2. Location of the ambient air sampling site (★) in Glendora.

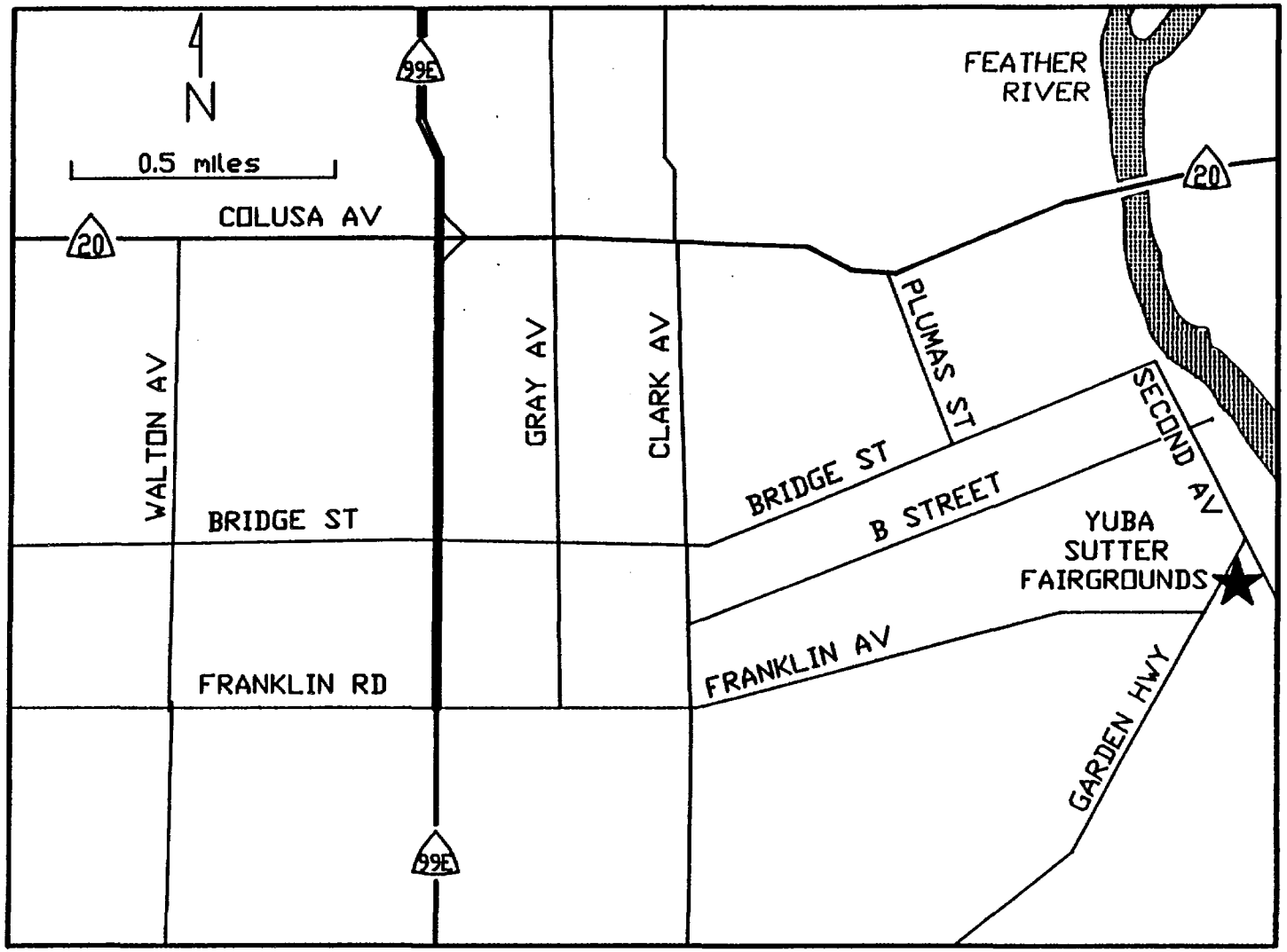


Figure III-3. Location of the ambient air sampling site (★) in Yuba City.

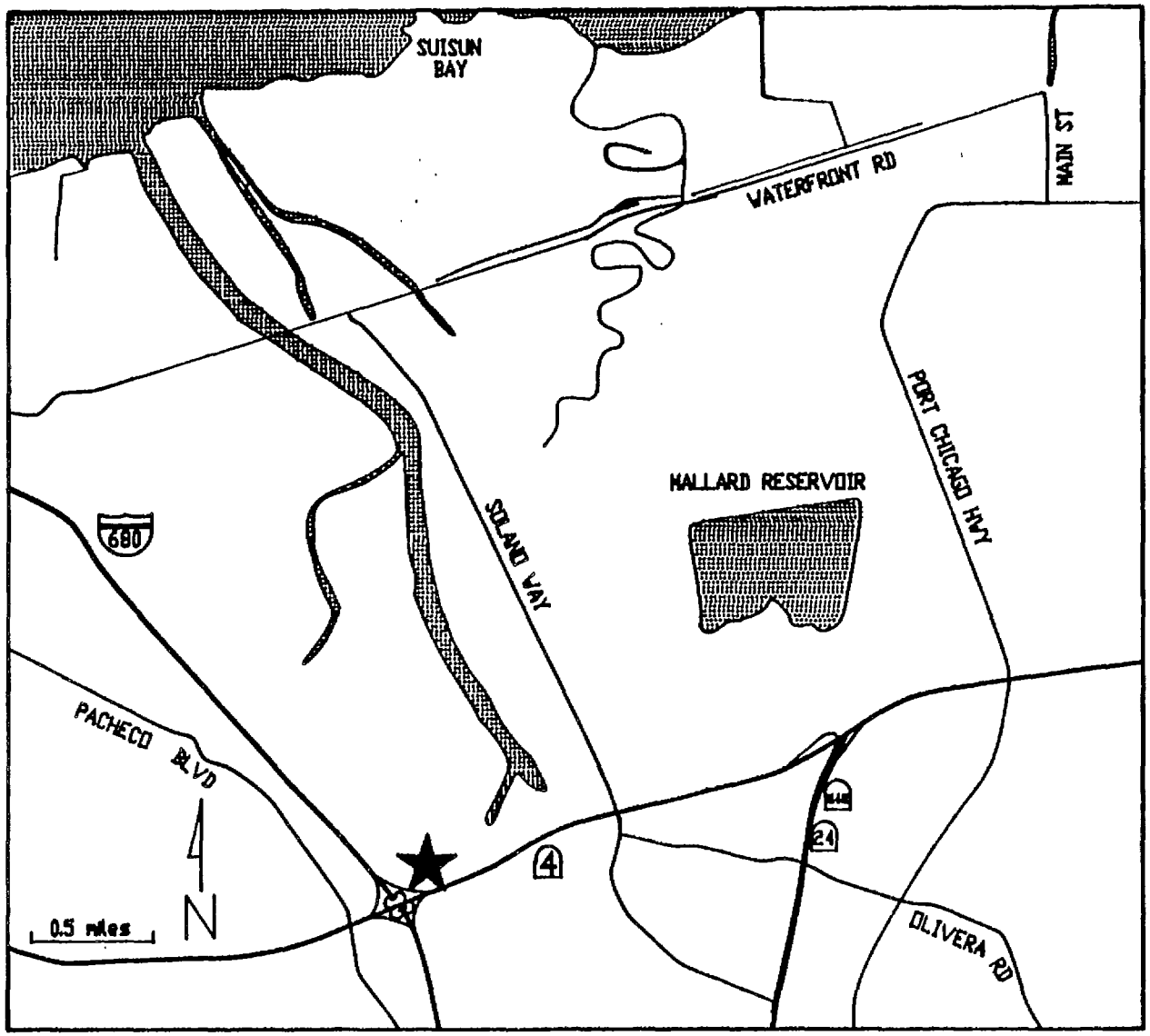


Figure III-4. Location of the ambient air sampling site (★) in Concord.

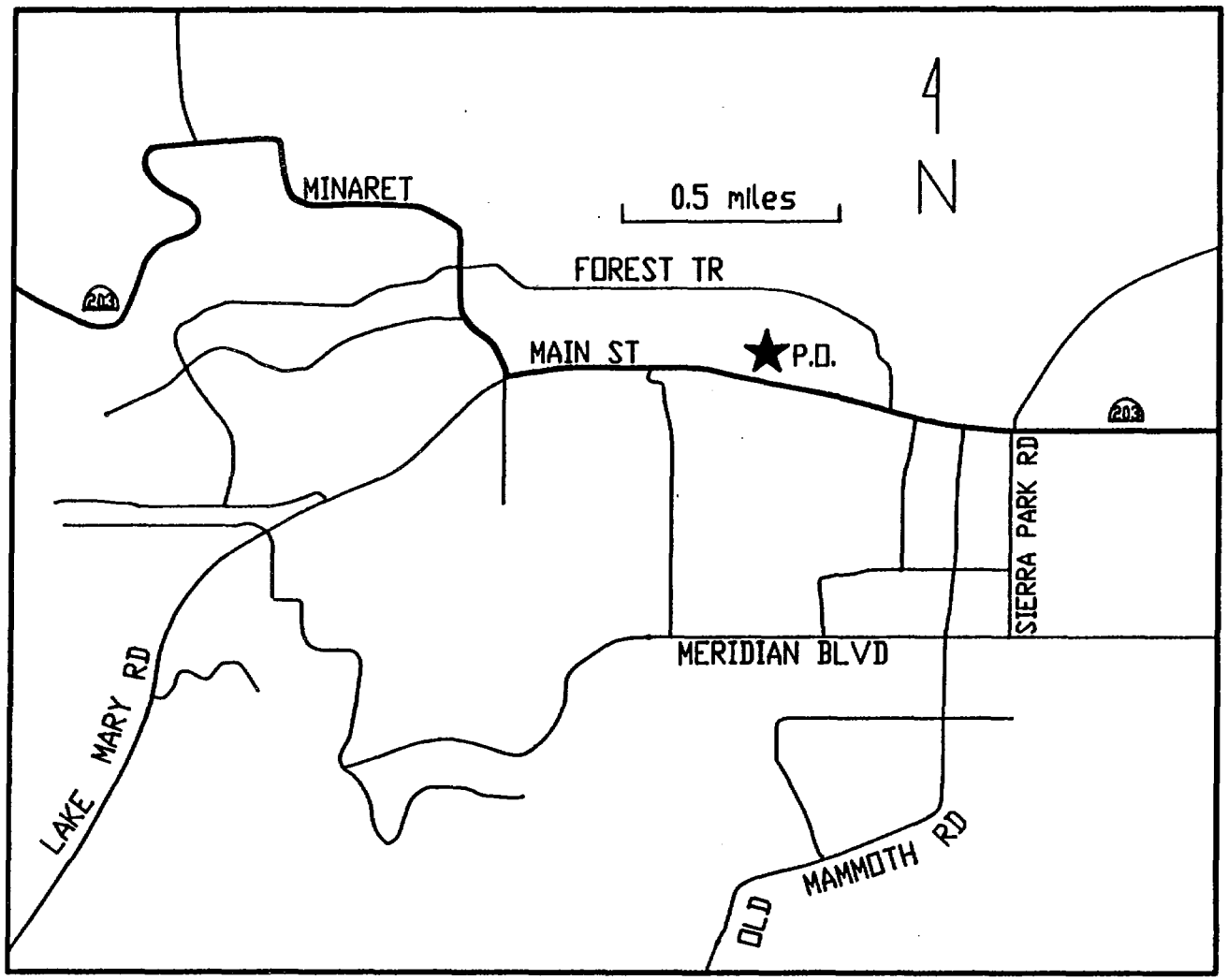


Figure III-5. Location of the ambient air sampling site (★) in Mammoth Lakes.

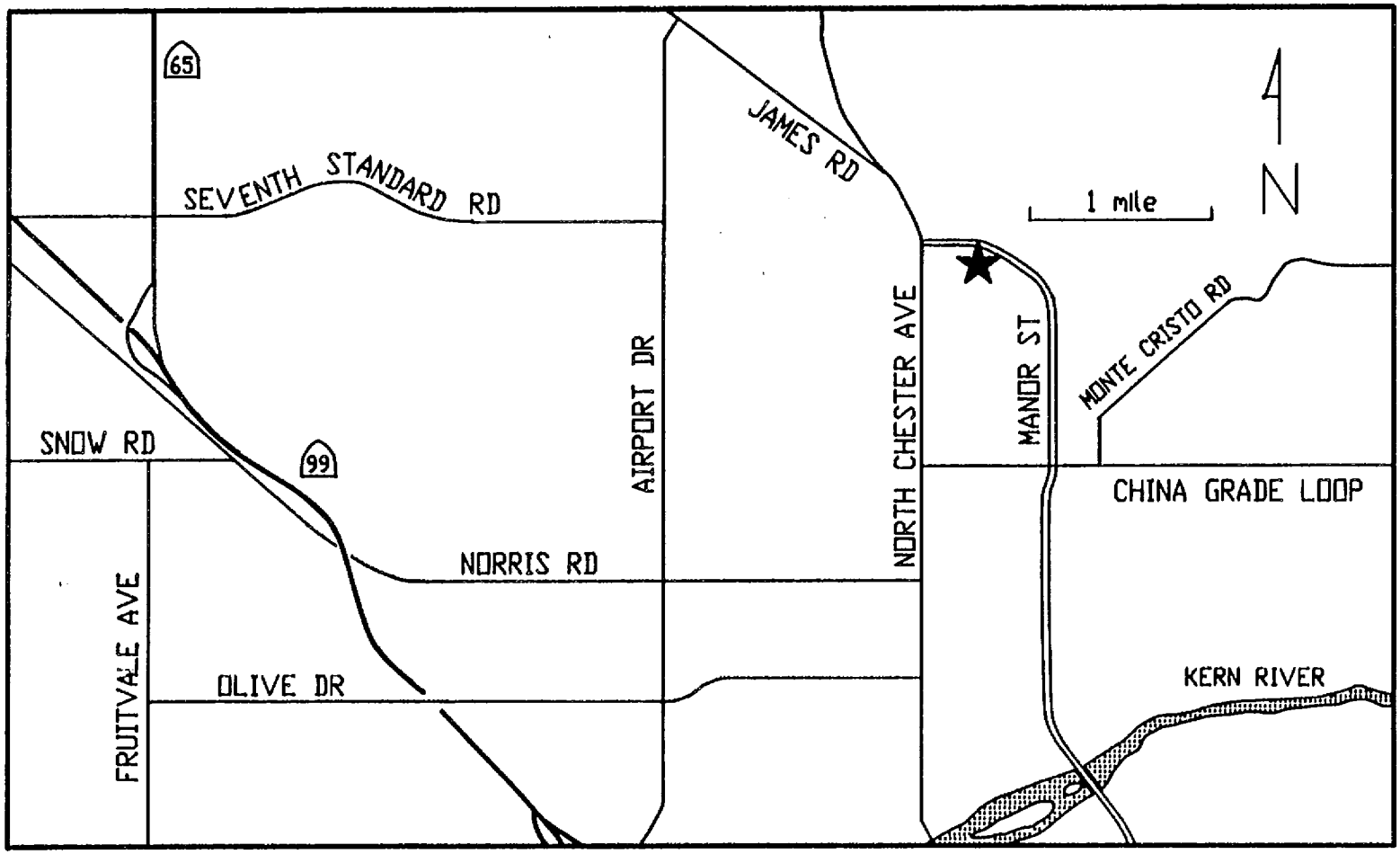


Figure III-6. Location of the ambient air sampling site (★) in Oildale.

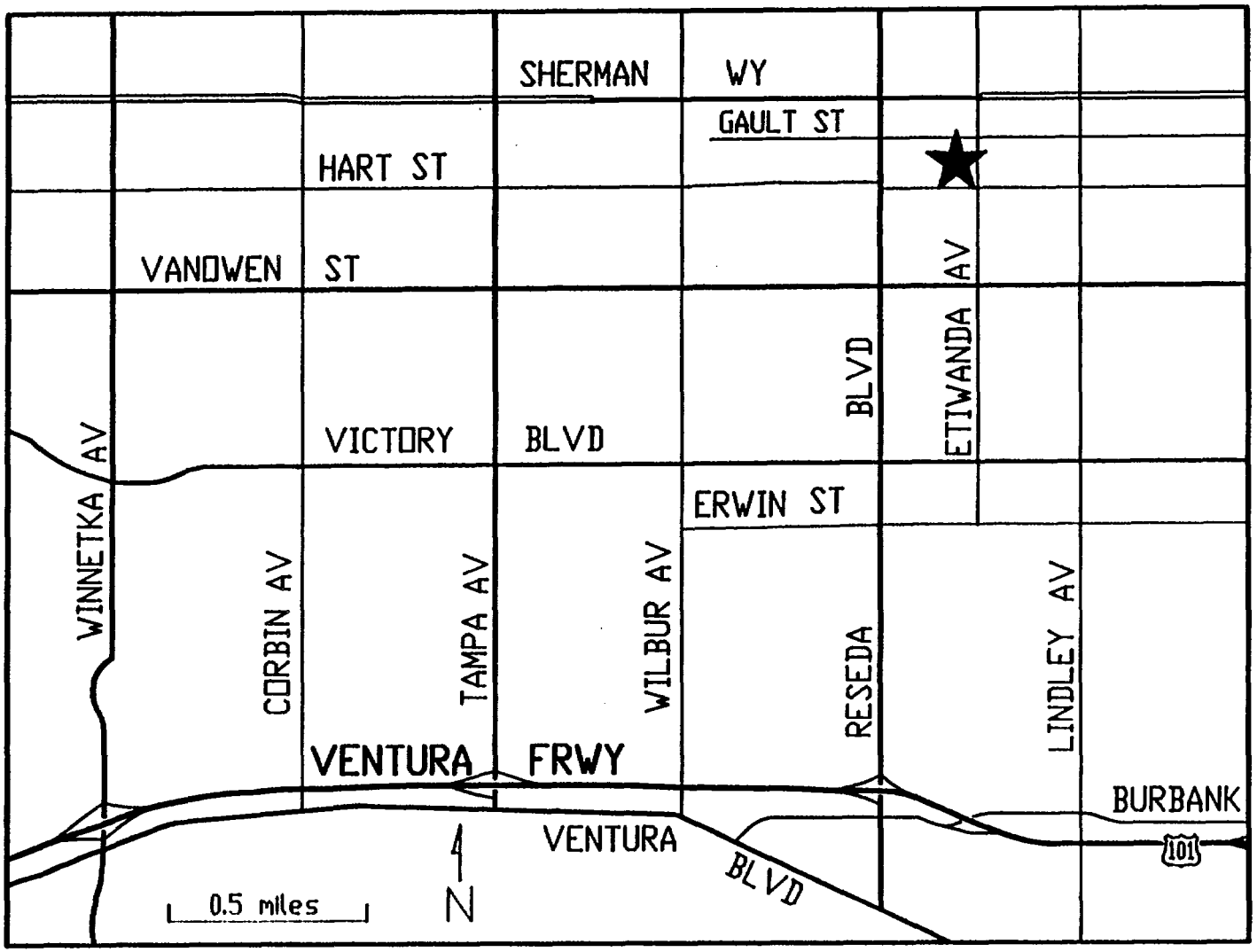


Figure III-7. Location of the ambient air sampling site (★) in Reseda.

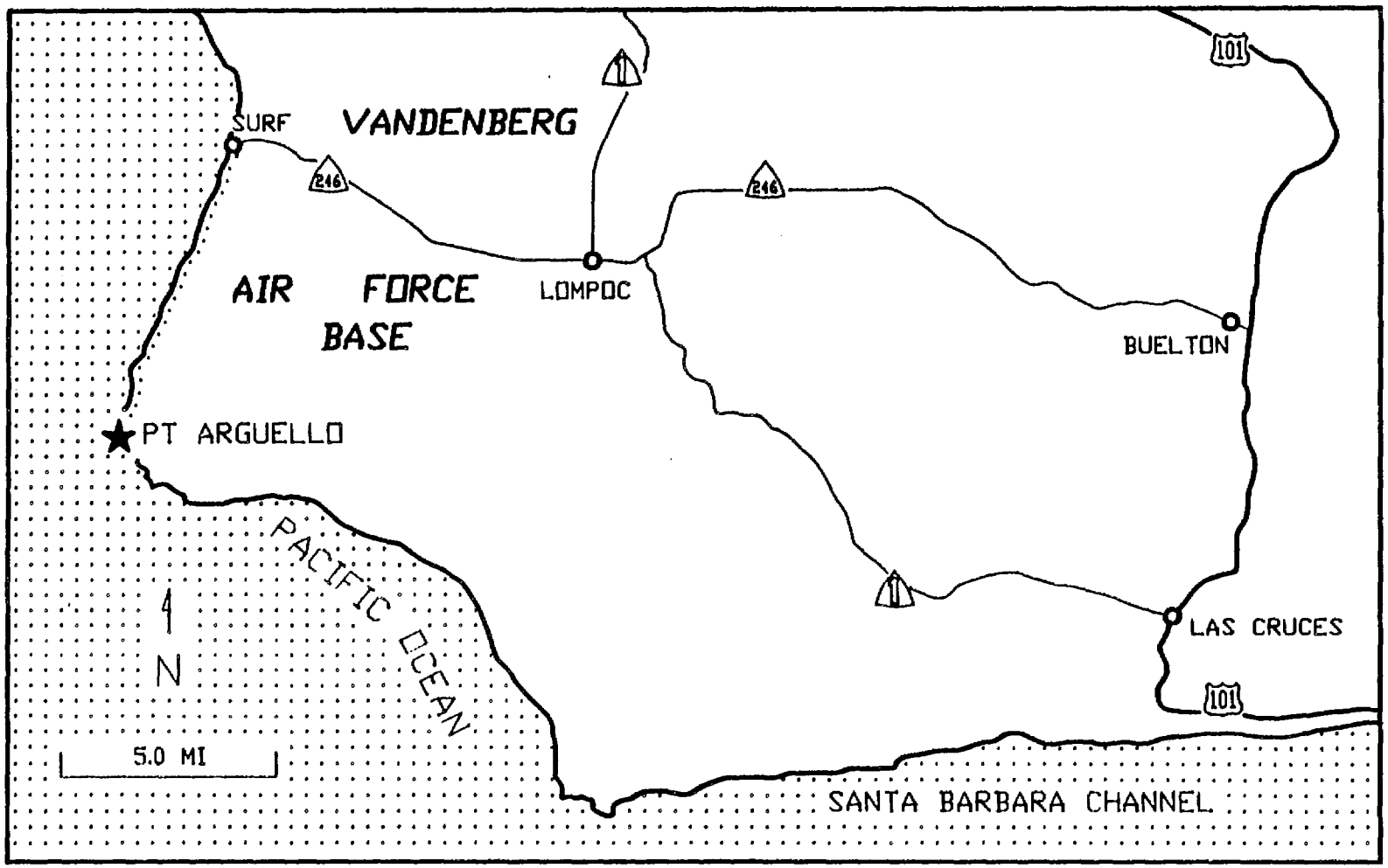


Figure III-8. Location (★) at which ambient air monitoring was carried out for the rural site.

Mammoth Lakes. The ambient air monitoring site in Mammoth Lakes (Figure III-5) was situated on the property of the Post Office, close to the fence between the Post Office and the Continental Telephone building. The samplers were located on a flat-bed trailer to elevate them above the snow level.

Oildale. Sampling at Oildale (Figure III-6) was carried out on the grounds of the ARB air monitoring station.

Reseda. Ambient air sampling at Reseda (Figure III-7) was carried out on the roof of the South Coast Air Quality Management District monitoring station at 18330 Gault Avenue. This flat roof was ~4 m above ground level, with an uninterrupted view in all directions.

Pt. Arguello. Sampling of ambient air was carried out at Pt. Arguello on Vandenberg Air Force Base (Figure III-8). The samplers were placed directly on bare ground on the Point, within sight of the Pacific Ocean.

B. Ambient Air Sampling Procedures

The PAH emitted from combustion sources exhibit a wide range of volatility, and are hence distributed in the atmosphere between the gas and particle phases. As we have shown previously (Arey et al. 1987), complementary sampling techniques are required to obtain a comprehensive data set concerning the concentrations of volatile and nonvolatile PAH and their derivatives in the atmosphere. Thus, the volatile two-ring PAH such as naphthalene, which are present almost entirely in the gas phase, can be quantitatively collected on Tenax-GC solid adsorbent. The nonvolatile five-ring and larger PAH and three- to four-ring nitroarenes are particle associated and are quantitatively collected on high-volume (Hi-vol) filters. The three- and four-ring PAH of intermediate volatility and the two-ring nitroarenes have been collected on polyurethane foam (PUF) plugs located downstream of the Hi-vol filters, indicating that they are either present mainly in the gas phase or are "blown off" the filters during the collection period (Arey et al. 1987). Thus, three different collection media, Tenax-GC solid adsorbent, PUF plugs and Hi-vol filters, were employed for ambient air sampling at Glendora, Yuba City, Concord, Mammoth Lakes, Oildale, Reseda and Pt. Arguello. For the ambient air sampling

carried out at San Nicolas Island, only Teflon-impregnated glass fiber (TIGF) filters were used to collect particulate matter.

1. Tenax-GC Cartridges

Prior to use, the Tenax-GC solid adsorbent was cleaned by Soxhlet extraction in a cellulose thimble for ~5 hr in a 6/4 (v/v) acetone/hexane mixture. After packing in Pyrex tubes (using precleaned glass wool), the Tenax cartridges were conditioned for ~4 hr by heating at 275°C with nitrogen flowing through them at ~20 mL min^{-1}. Two sizes of Tenax-GC cartridge were used for the collection of gas-phase PAH at different flow rates. The "low-flow" cartridges consisted of 10 cm x 4 mm i.d. Pyrex tubes packed with 0.1 g of Tenax-GC solid adsorbent. A sampling flow rate of ~1 L min^{-1} was employed, yielding an ~0.6 m^3 volume of air sampled for each 12-hr period. The "high-flow" cartridges consisted of 10 cm x 1 cm i.d. Pyrex tubes packed with 0.6 g of Tenax-GC. These were operated at a flow rate of ~10 L min^{-1}, resulting in ~6 m^3 of air sampled during a 12-hr period. At each sampling location, selected low-flow cartridges were equipped with a back-up Tenax cartridge placed in series downstream from the first cartridge to check for breakthrough. The flow rates were measured at the beginning and end of each sampling period and were adjusted at the beginning of each sampling period, using calibrated rotameters. After sampling, the Tenax cartridges were placed in capped glass test tubes and placed on dry ice until transported to a laboratory freezer.

2. Hi-Vol Filters Followed by PUF Plugs

The Teflon-impregnated glass fiber (TIGF) filters (Pallflex T60A20) and PUF plugs were cleaned by Soxhlet extraction for ~16 hr in methylene chloride, followed by another 16-hr extraction with methanol. Two Hi-vol sampler systems consisting of a TIGF filter followed by three (or four in the case of sampling at Glendora) PUF plugs (each being ~9 cm diameter x 5 cm thick) [see Figure III-9] were operated at ~25 SCFM for 12-hr intervals, yielding ambient samples collected from ~1000 m^3 of air. These modified Hi-vol sampler systems were not equipped with a cut-off inlet. The four PUF plugs from each of the two modified Hi-vols at Glendora were individually wrapped in aluminum foil following sampling and immediately placed on dry ice until transported to a laboratory freezer. At each of the subsequent sampling sites, each set of three PUF plugs was

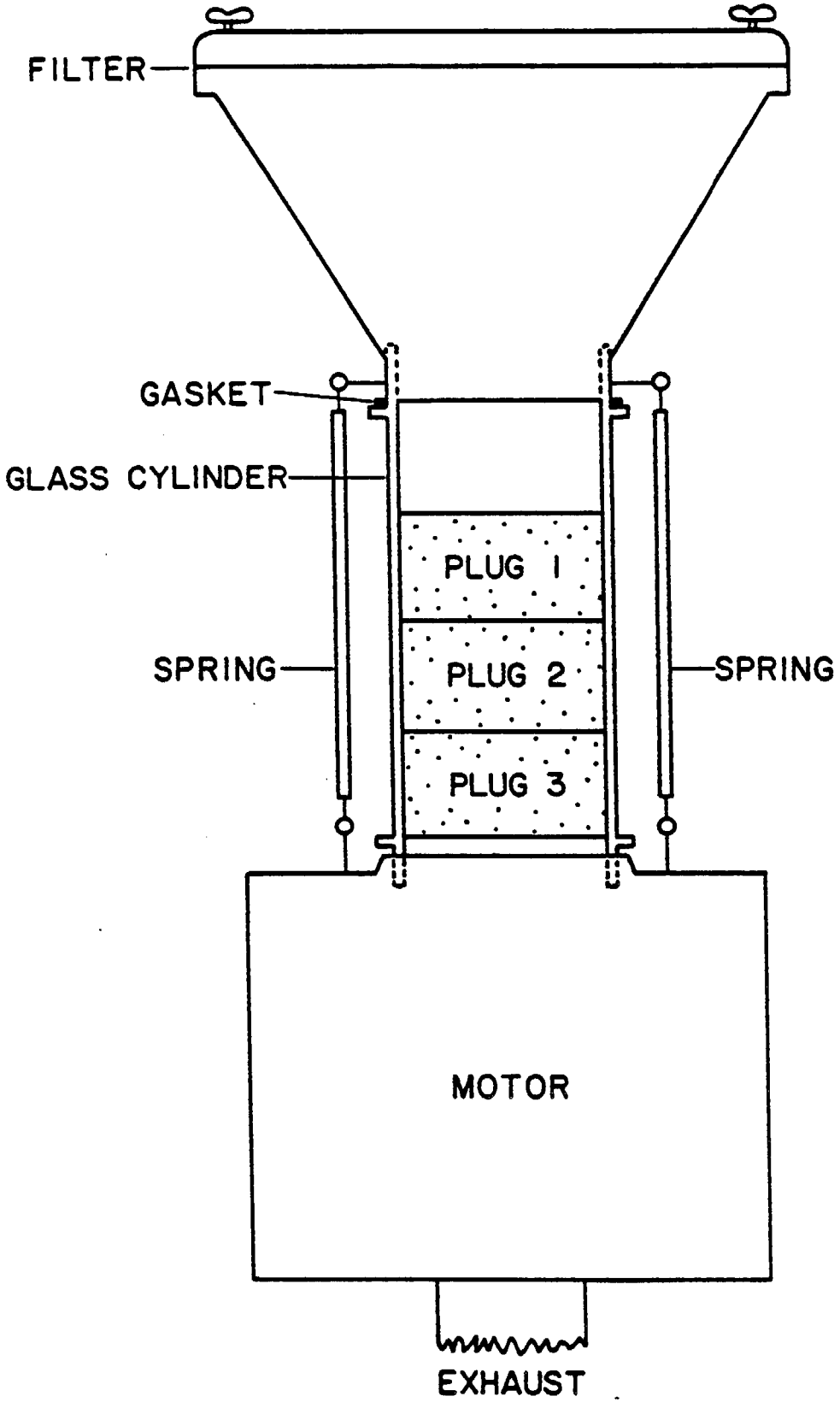


Figure III-9. Schematic of modified Hi-vol sampler with PUF plugs underneath the filter to collect gas-phase species and compounds "blown off" the filter.

placed in a Mason canning jar equipped with a Teflon gasket prior to cooling with dry ice. The TIGF filters were treated as described below.

3. Hi-Vols with TIGF Filters: Sampling and Analysis

Six or seven Hi-vol samplers, each equipped with a 10 μm cut-off inlet (in order to collect particles in the respirable range), were employed for particle collection for mutagenicity testing and chemical analysis. The particles were collected on precleaned (as above), pre-weighed TIGF filters in samplers run at ~40 SCFM, yielding an ambient sample collected from ~800 m^3 of air for each Hi-vol over a 12-hr sampling period. Two of these Hi-vol samplers were employed solely for the collection of particulate matter used for mutagenicity testing. The Pallflex T60A20 TIGF filters used had a stated collection efficiency >90% for particles down to 0.3 μm at the face velocities employed. While the stated minimum collection efficiency is 60% at 0.1 μm, the collection efficiency for this size fraction was expected to increase rapidly as particles are collected on the filter.

After each sample collection, all particle-laden filters were individually wrapped in aluminum foil, placed in manila envelopes and stored at dry ice temperature and then at freezer temperatures until extraction (the sole exception was that approximately half of the particle-laden filters from San Nicolas Island were not maintained at dry ice temperature prior to reaching Riverside).

The flow rates of the Hi-vol samplers were calibrated by SAPRC personnel at all of the sites except San Nicolas Island (for which the sampler was calibrated by the staff of AeroVironment) at the beginning and end of each sampling episode. In addition, for all of the sites except San Nicolas Island, an independent calibration of the Hi-vol samplers was carried out by a different member of the SAPRC research group during the sampling period. These calibrations were conducted using an orifice calibrator, and for the flow rate measurements at Mammoth Lakes, corrections were made for the low temperatures (typically around 0°C) and low barometric pressures [~580 Torr (mm Hg)] encountered (although the effects of the temperature and pressure corrections canceled out to a large extent) using the manufacturer's calibration of flow rate against $[\Delta H(P/760)\{298/(273 + T)\}]^{\frac{1}{2}}$, where P is the ambient pressure in mm Hg, T is temperature in °C and ΔH is the orifice pressure drop in inches

IV. RESULTS OF MUTAGENICITY TESTING

A. Introduction

Under previous research support from the ARB, we have shown that organic extracts of respirable ambient particulate matter are directly mutagenic in the Salmonella mutagenicity test of Ames, and that this mutagenic activity is associated primarily with particles in the sub-micron or "respirable" size range. Although our previous research has focused on particulate matter collected in California's South Coast Air Basin, other researchers have made similar observations, and it is now generally accepted that mutagenic particulate matter is characteristic of polluted urban atmospheres worldwide. Some of this mutagenic activity is associated with direct emissions from combustion sources such as diesel and gasoline engines (Huisingh et al. 1978, Löfroth 1981, Lewtas 1982, Pierson et al. 1983). Moreover, the direct activity of motor vehicle POM, both from gasoline and diesel engines, has been shown to correlate with mammalian cell mutagenesis and skin tumor initiation assays (Lewtas 1983).

For ambient POM collected in southern California, we have found that up to ~10% of the mutagenic activity can be attributed to mutagenic nitroarenes (predominantly 2-nitrofluoranthene) which are not present in combustion emissions, but are a product of the atmospheric reactions of the parent PAH. The potential health hazards of nitroarenes, which are known to contribute to the direct mutagenic activity of vehicle POM, particularly that from diesel-fueled vehicles, has recently been reviewed (Tokiwa and Oshnishi 1986). The mutagenicity of ambient POM, sampled under various ambient atmospheric regimes in California, should provide information concerning the nature and degree of these potential carcinogenic hazards and, when combined with data on the ambient concentrations of the PAH and their derivatives, insights into their sources.

B. Experimental

Sample preparation for mutagenicity testing. As noted in Section III, the filters from two Hi-vols with 10 μm inlets were set aside for mutagenicity testing. It was assumed that for all sites, with the

exception of Pt. Arguello, sufficient material would be present from two simultaneous filter samples during a 12-hr period to allow a full mutagenicity test (i.e., with a full dose-response curve). The particulate matter was weighed, and the filters extracted by a 16-hr Soxhlet extraction using a benzene/methanol (80/20) azeotrope. The solvent was removed under vacuum and the extracts were taken to dryness under a stream of dry nitrogen. Prior to mutagenicity testing, the samples were stored in the dark at -75°C. The day of the test, each extract was dissolved in dimethylsulfoxide (DMSO) using a 20-min sonication, and serial dilutions in DMSO were made from this stock solution.

The samples from the rural site at Pt. Arguello, Vandenberg Air Force Base, were treated in a slightly different manner because of their low expected mutagenicity. A preliminary test of one of these filters chosen at random indicated that pooling of samples would be necessary to obtain a detectable mutagenic response. Two nighttime and two daytime samples were obtained by pooling the particulate matter collected on five consecutive days. Because visual inspection revealed that a large portion of each extract consisted of inorganic salts, the DMSO stock solution was centrifuged to sediment any undissolved salts just prior to serial dilution in DMSO. Additionally, because it was felt that the extract weight was not indicative of the amount of organic matter collected, each of the four samples in this set were tested at higher doses which were based on equivalent sampling volumes rather than equivalent extract weights. The large amount of inorganic matter in these samples should be considered when comparing the specific activities (extract potencies) and mutagen loadings (particulate potencies) from this site with those of other sites.

Tester strains. TA98 was used because of its sensitivity to atmospheric particulate mutagens such as the nitroarenes (Rosenkranz and Mermelstein 1983), and each particulate extract was tested on this strain both in the presence and in the absence of mammalian metabolic activation (S9). Each sample was also tested on strains TA98NR and TA98/1,8-DNP_6 in the absence of S9. TA98NR and TA98/1,8-DNP are isolates of TA98 which are deficient in a nitroreductase (Rosenkranz and Speck 1975, McCoy et al. 1981) and a transacetylase enzyme, respectively. The deficiency of these enzymes, which are required in the activation of many nitroarenes to penultimate mutagens, renders these strains less sensitive than TA98 to

of H_2O. As far as possible, the recommendations of the Ambient Air Quality Surveillance document [40 CFR Ch. 1 (7-1-85 Edition)] regarding siting of the Hi-vol samplers and their operation were followed.

Table IV-1. Response of TA98NR and TA98/1,8-DNP_6 Relative to TA98 for Standard Nitroarenes

Compound	Ratios of Response (-S9)	
	TA98NR to TA98	TA98/1,8-DNP_6 to TA98
2-Nitrofluoranthene	0.24	0.17
3-Nitrofluoranthene	0.49	0.13
8-Nitrofluoranthene	0.33	0.30
1-Nitropyrene	0.13	0.57
2-Nitropyrene	0.10	0.14
1,8-Dinitropyrene	1.0	0.021

many mutagenic nitroarenes. Thus, when a complex mixture exhibits less activity on TA98NR or TA98/1,8-DNP_6, relative to TA98, it may be an indication of the contribution of nitroarenes to mutagenic activity of that sample. Table IV-1 shows the response of TA98NR and TA98/1,8-DNP_6, relative to TA98, that we have obtained for several mutagenic atmospheric nitroarenes.

The strains were cultured in 40 mL of L-broth for 12 hr at 37°C with shaking (120 rpm). The culture density was estimated by its absorbance at 550 nm, and each strain was diluted with fresh medium to an absorbance (~0.28) previously calculated to yield the standard culture density of 10^9 colony-forming units per mL. After dilution, the cultures were maintained in an ice bath for the duration of the test. The titer of each culture was determined by dilution and plating on histidine-supplemented medium E. The standard genotypic markers which were routinely checked were: crystal violet sensitivity, UV sensitivity and ampicillin resistance. Three standard positive-control mutagens were tested on each strain: (1) 2-nitrofluorene, a positive control mutagen which we have used for 10 years to check the response of TA98, was also used to check the reduced response of TA98NR relative to TA98; (2) 1,8-dinitropyrene was used to check the reduced response of TA98/1,8-DNP_6 relative to TA98 and TA98NR

for nitroarenes which require the Salmonella transacetylase for activation and (3) quercetin was used to check the equivalent response of these strains to non-nitroarene mutagens. Additionally, benzo[a]pyrene was tested on TA98 (+S9) to check the response of this strain to promutagens.

S9. Arochlor 1254-induced rat liver S9 was prepared by Litton Bionetics, Inc., according to the method of Ames et al. (1975) and contained 25 mg mL^{-1} protein (manufacturer's analysis). NADP was purchased from Boehringer Mannheim and glucose-6-phosphate was purchased from Sigma Chemical Company.

The S9 mix was prepared by the standard protocol (Ames et al. 1975, Maron and Ames 1983), with 0.01 mL S9 per plate (2% v/v mix). This S9 concentration was chosen because we have previously found a 2% v/v mix to be optimal in activating ambient particulate extracts collected in southern California. Frequently, the use of S9 in testing ambient POM results in a net decrease in activity, as deactivation of direct mutagens overrides the presumed activation of indirect mutagens, such as the PAH. Many nitroarenes are subject to this S9 suppression of activity.

Testing protocol. The standard Ames Salmonella plate incorporation mutagenicity test was performed according to the method of Ames and co-workers (Ames et al. 1975, Maron and Ames 1983) with some modifications to improve the accuracy and precision of the test (Belser et al. 1981). Because of the large number of plates needed to test most sample sets, the extracts from each site were generally tested in two tests: TA98 with and without S9, and TA98NR and TA98/1,8-DNP (both without S9). By dividing the tests by strain, it was felt that the variation in response within one sample set would be minimized. Each extract was tested in triplicate at eight doses chosen to logarithmically span the region of linear response observed in the past for ambient POM. In anticipation of lower activities on TA98NR and TA98/1,8-DNP_6, the doses chosen for these strains were twice as great as those for TA98. Hence each sample was tested at 3, 6, 11, 21, 38, 70, 135 and 250 µg plate on TA98 and at 6, 12, 22, 42, 76, 140, 270 and 500 µg plate on TA98NR and TA98/1,8-DNP_6.

Each test was performed in a single afternoon using a procedure designed to improve intraday precision (Belser et al. 1981). Darkroom conditions were employed throughout to prevent any photodecomposition of the samples. The plates were incubated at 37°C for 63 hr and counted with

a Biotran automatic colony counter (New Brunswick Scientific) directly interfaced to a microcomputer (Apple II). The extract potencies, or specific activities, were obtained by linear regression analysis of the dose-response data in the region of linear response. The slope of the dose-response curve is the specific activity, in revertants μg^{-1}. As discussed above, the ratios of the specific activities on strains TA98NR and TA98/1,8-DNP_6 relative to TA98 were then calculated as an indication of the contribution of nitroarenes to the mutagenicity of each extract.

From the specific activities, the extract weights, and the weights of the particulate matter collected, the potencies of the particulate matter, or mutagen loadings in revertants per mg of particulate matter collected, were calculated. Finally, from the specific activities, the extract weights, and the volumes of sampled air, the airborne mutagenicity "concentrations", or mutagen densities in revertants per m^3 of sampled air, were calculated.

C. Results

Our testing protocol consistently results in somewhat higher mutagenicities than other laboratories, which we attribute primarily to the use of L-broth instead of Oxoid broth to culture the tester strains. L-broth has approximately twice the histidine as Oxoid, and its use results in larger amounts of histidine on the test plate. Because it is the limiting growth factor, a higher amount of histidine results in a higher number of cells on the test plate and hence a higher number of revertants (Maron and Ames 1983). The use of L-broth also results in a somewhat heavier background lawn of unreverted Salmonella, but colony morphology and visibility are unaffected.

The interday reproducibility of our testing procedure can be seen from Table IV-2 which lists the specific activities obtained for the standard control mutagens tested with each sample group. This table also shows the generally high sensitivity achieved with our testing protocol. Compare, for example, our values for 2-nitrofluorene on TA98(-S9) with those of other investigators given in footnote b, Table IV-2. The results of the mutagenicity tests are contained in Tables IV-3 through IV-9, with each table containing the results from one sampling site. These tables are subdivided into four parts: (A) sampling data (including total

Table IV-2. Mutagenicities of Standard Control Mutagens for Individual Sample Tests

Sample Group	Test Date	Salmonella Strains	Specific Activities (rev μg^{-1}) Benzo-[a]-pyrene (+S9)	2-Nitro-fluorene[b] (-S9)	Quer-cetin (-S9)	1,8-Dinitro-pyrene (-S9)
Glendora	2/23/87	TA98	330	460	13	1.1×10^6
	3/2/87	TA98NR	a	69	15	1.1×10^6
	3/2/87	TA98DNP	a	90	14	29,000
Yuba City	5/25/87	TA98	390	520	16	1.3×10^6
	4/27/87	TA98NR	a	88	18	1.5×10^6
	5/3/87	TA98DNP	a	100	17	26,000
Concord	6/28/87	TA98	320	480	11	8.8×10^5
	6/21/87	TA98NR	a	50	14	8.8×10^5
	6/30/87	TA98DNP	a	61	12	20,000
Mammoth Lakes	7/24/87	TA98	290	440	12	1.0×10^6
	7/13/87	TA98NR	a	31	12	9.2×10^5
	7/20/87	TA98DNP	a	63	13	20,000
Oildale	8/24/87	TA98	320	440	11	8.9×10^5
	8/17/87	TA98NR	a	34	12	7.8×10^5
	8/17/87	TA98DNP	a	82	10	17,000
Reseda	9/25/87	TA98	360	510	11	1.2×10^6
	8/31/87	TA98NR	a	36	13	1.1×10^6
	9/18/87	TA98DNP	a	71	9.8	23,000
Pt. Arguello	10/22/87	TA98	350	420	11	1.2×10^6
	10/22/87	TA98NR	a	42	9.9	1.1×10^6
	10/22/87	TA98DNP	a	94	9.9	24,000

[a]Benzo[a]pyrene was tested with S9 on TA98 only.
[b]Average value for 2-nitrofluorene (rev μg^{-1}) on TA98 reported by other laboratories is 183 ± 36 rev μg^{-1} (Tokiwa and Ohnishi 1986).

Table IV-3A. Particulate Data for 12-Hr Collections at Glendora, August 1986

Date	Time of Day (PDT)	Particulate Weight; 2 Filters (mg)	TSP ($\mu g\ m^{-3}$)[a]	Extract Weight (mg)	% Extractable[b]
8/12/86	0800-2000	200.4	130[c]	48.39	24
8/12-13/86	2000-0800	115.6	71	50.28	43
8/13/86	0800-2000	208.8	130	57.61	28
8/13-14/86	2000-0800	134.4	82	59.54	44
8/14/86	0800-2000	233.3	140	64.84	28
8/14-15/86	2000-0800	106.8	65	31.42	29
8/15/86	0800-2000	185.5	110	55.81	30
8/15-16/86	2000-0800	107.3	66	33.61	31
8/16/86	0800-2000	152.6	94	53.66	35
8/16-17/86	2000-0800	96.0	59	46.65	49
8/17/86	0800-2000	134.7	83	52.03	39
8/17-18/86	2000-0800	92.4	57	28.10	30
8/18/86	0800-2000	210.7	130	42.87	20
8/18-19/86	2000-0800	93.7	57	18.81	20
8/19/86	0800-2000	169.5	100	41.08	24
8/19-20/86	2000-0800	97.2	60	36.61	38
8/20/86	0800-2000	188.4	120	49.69	26
8/20-21/86	2000-0800	117.1	72	28.46	24

[a]Flow rates for the two samples (Hi-vols #8 and #11) were 40 SCFM for a total sampling volume of 1631 m^3.
[b]16-hr Soxhlet extraction with benzene/methanol (80/20).
[c]Sampling volume ~5% low due to power failure.

Table IV-3B. Specific Activities of Particulate Extracts Collected at Glendora, August 1986

Date	Time of Day (PDT)	Specific Activity (rev μg^{-1})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9	Ratios of Response (-S9) TA98NR to TA98	TA98/ 1,8-DNP_6 to TA98
8/12/86	0800-2000	1.4 (1.8)	1.3 (3.5)	0.58 (2.4)	0.31 (5.8)	0.45	0.24
8/12-13/86	2000-0800	1.0 (2.0)	0.97 (2.2)	0.50 (3.0)	0.21 (7.1)	0.52	0.22
8/13/86	0800-2000	0.77 (1.1)	0.63 (3.2)	0.22 (5.5)	0.093 (8.5)	0.35	0.15
8/13-14/86	2000-0800	1.2 (2.6)	1.2 (1.3)	0.68 (1.4)	0.27 (5.9)	0.57	0.23
8/14/86	0800-2000	0.82 (1.1)	0.87 (4.0)	0.38 (3.2)	0.17 (8.8)	0.44	0.20
8/14-15/86	2000-0800	0.78 (4.0)	0.57 (2.1)	0.34 (2.5)	0.18 (6.1)	0.60	0.32
8/15/86	0800-2000	0.82 (2.1)	0.80 (2.3)	0.31 (3.9)	0.15 (9.3)	0.39	0.19
8/15-16/86	2000-0800	1.5 (0.7)	2.0 (3.1)	1.0 (2.2)	0.47 (4.9)	0.50	0.24
8/16/86	0800-2000	0.84 (2.4)	0.87 (3.4)	0.35 (6.0)	0.15 (13)	0.40	0.17
8/16-17/86	2000-0800	1.4 (2.0)	1.4 (2.9)	0.66 (2.7)	0.29 (2.8)	0.47	0.21
8/17/86	0800-2000	0.86 (2.0)	0.84 (3.1)	0.35 (4.0)	0.14 (14)	0.42	0.17
8/17-18/86	2000-0800	2.3 (1.8)	2.5 (4.0)	1.3 (3.0)	0.55 (3.1)	0.52	0.22
8/18/86	0800-2000	1.6 (1.8)	2.0 (3.3)	0.87 (4.0)	0.29 (5.2)	0.44	0.15
8/18-19/86	2000-0800	1.3 (3.0)	1.1 (2.7)	0.64 (2.8)	0.25 (6.0)	0.58	0.23
8/19/86	0800-2000	1.3 (1.7)	1.4 (5.4)	0.48 (3.1)	0.21 (7.1)	0.34	0.15
8/19-20/86	2000-0800	1.7 (3.2)	1.9 (1.8)	0.81 (2.1)	0.38 (6.3)	0.43	0.20
8/20/86	0800-2000	1.8 (2.6)	2.0 (7.0)	0.69 (3.3)	0.34 (2.6)	0.35	0.17
8/20-21/86	2000-0800	1.6 (2.4)	1.6 (3.3)	0.73 (9.2)	0.31 (4.2)	0.46	0.19

[a]Slope of the dose-response curve in the region of linear response. The number in parentheses is the standard error expressed as a percentage of the specific activity.

Table IV-3C. Mutagen Loadings of Particulate Matter Collected at Glendora, August 1986

Date	Time of Day (PDT)	Mutagen Loading (rev mg^{-1})			
		TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
8/12/86	0800-2000	340	300	140	75
8/12-13/86	2000-0800	430	420	220	91
8/13/86	0800-2000	210	170	61	26
8/13-14/86	2000-0800	530	530	300	120
8/14/86	0800-2000	230	240	110	47
8/14-15/86	2000-0800	230	170	100	53
8/15/86	0800-2000	250	240	93	45
8/15-16/86	2000-0800	470	630	310	150
8/16/86	0800-2000	300	310	120	53
8/16-17/86	2000-0800	680	680	320	140
8/17/86	0800-2000	330	320	140	54
8/17-18/86	2000-0800	700	760	400	170
8/18/86	0800-2000	330	410	180	59
8/18-19/86	2000-0800	260	220	130	50
8/19/86	0800-2000	320	340	120	51
8/19-20/86	2000-0800	640	720	310	140
8/20/86	0800-2000	470	530	180	90
8/20-21/86	2000-0800	390	390	180	75

Table IV-3D. Particulate Mutagen Densities, Glendora, August 1986

Date	Time of Day (PDT)	Mutagen Density (rev m^{-3})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP$_6$ -S9
8/12/86	0800-2000	42[b]	39[b]	17[b]	9.2[b]
8/12-13/86	2000-0800	31	30	15	6.5
8/13/86	0800-2000	27	22	7.8	3.3
8/13-14/86	2000-0800	44	44	25	10
8/14/86	0800-2000	33	35	15	6.8
8/14-15/86	2000-0800	15	11	6.5	3.5
8/15/86	0800-2000	28	27	11	5.1
8/15-16/86	2000-0800	31	41	21	10
8/16/86	0800-2000	28	29	12	4.9
8/16-17/86	2000-0800	40	40	19	8.3
8/17/86	0800-2000	27	27	11	4.5
8/17-18/86	2000-0800	40	43	22	9.5
8/18/86	0800-2000	42	53	23	7.6
8/18-19/86	2000-0800	15	13	7.4	2.9
8/19/86	0800-2000	33	35	12	5.3
8/19-20/86	2000-0800	38	43	18	8.5
8/20/86	0800-2000	55	61	21	10
8/20-21/86	2000-0800	28	28	13	5.4

[a]Flow rates for the two samples (Hi-vols #8 and #11) were 40 SCFM for a total sampling volume of 1631 m^3.
[b]Sampling volume ~5% low due to power failure.

Table IV-4A. Particulate Data for 12-Hr Collections at Yuba City, October 1986

Date	Time of Day (PDT)	Particulate Weight; 2 Filters (mg)	TSP ($\mu g\ m^{-3}$)[a]	Extract Weight (mg)	% Extractable[b]
10/16/86	0700-1900	146.4	91	43.28	30
10/16-17/86	1900-0700	47.6	29	13.57	29
10/17/86	0700-1700	63.9	47	21.39	33
10/18/86	0700-1900	46.1	28	16.54	36
10/18-19/86	1900-0700	20.8	13	11.22	54
10/20/86	0900-1900	85.3	63	31.15	37
10/20-21/86	1900-0700	106.0	66	48.30	46
10/21/86	0700-1900	109.5	68	28.59	26
10/21-22/86	1900-0700	101.0	63	36.90	37
10/23/86	0830-1620	100.1	96	47.47	47
10/23-24/86	2330-0730	49.3	46	21.01	43
10/25/86	1000-1700	41.1	44	11.91	29

[a]Average flow rates for the two samplers were 40.4 SCFM (Hi-vol #8) and 38.7 SCFM (Hi-vol #11) for a total sampling volume of 1612 m^3.
[b]16-hr Soxhlet extraction with benzene/methanol (80/20).

Table IV-4B. Specific Activities of Particulate Extracts Collected at Yuba City, October 1986

Date	Time of Day (PDT)	Specific Activity (rev μg^{-1})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9	Ratios of Response (-S9) TA98NR to TA98	TA98/ 1,8-DNP_6 to TA98
10/16/86	0700-1900	0.65 (9.4)	0.89 (3.5)	0.36 (5.1)	0.13 (7.4)	0.40	0.15
10/16-17/86	1900-0700	0.33 (8.9)	0.51 (11)	0.32 (5.9)	0.18 (5.6)	0.63	0.35
10/17/86	0700-1700	1.6 (6.8)	1.5 (4.5)	0.76 (4.0)	0.31 (9.1)	0.51	0.21
10/18/86	0700-1900	1.0 (3.2)	0.76 (4.2)	0.41 (4.8)	0.14 (11)	0.54	0.18
10/18-19/86	1900-0700	1.1 (6.0)	0.90 (8.8)	0.38 (4.8)	0.26 (5.5)	0.42	0.29
10/20/86	0900-1900	0.63 (9.6)	0.46 (5.8)	0.17 (6.4)	0.092 (13)	0.37	0.20
10/20-21/86	1900-0700	1.2 (6.6)	1.2 (3.4)	0.75 (4.2)	0.30 (6.3)	0.63	0.25
10/21/86	0700-1900	1.6 (6.3)	2.6 (3.3)	1.3 (3.0)	0.53 (9.0)	0.50	0.20
10/21-22/86	1900-0700	1.7 (3.4)	2.6 (3.6)	1.4 (5.8)	0.63 (4.8)	0.54	0.24
10/23/86	0830-1620	1.8 (4.7)	2.1 (3.6)	1.1 (4.3)	0.41 (5.1)	0.52	0.20
10/23-24/86	2330-0730	2.1 (2.4)	2.9 (9.7)	1.5 (3.2)	0.76 (3.6)	0.52	0.26
10/25/86	1000-1700	0.44 (9.7)	0.58 (4.9)	0.17 (12)	0.073 (14)	0.29	0.13

[a]Slope of the dose-response curve in the region of linear response. The number in parentheses is the standard error expressed as a percentage of the specific activity.

Table IV-4C. Mutagen Loadings of Particulate Matter Collected at Yuba City, October 1986

Date	Time of Day (PDT)	Mutagen Loading (rev mg^{-1}) TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
10/16/86	0700-1900	190	260	110	38
10/16-17/86	1900-0700	94	150	91	51
10/17/86	0700-1700	540	500	250	100
10/18/86	0700-1900	360	270	150	50
10/18-19/86	1900-0700	590	490	200	140
10/20/86	0900-1900	230	170	62	34
10/20-21/86	1900-0700	550	550	340	140
10/21/86	0700-1900	420	680	340	140
10/21-22/86	1900-0700	620	950	510	230
10/23/86	0830-1620	850	1000	520	190
10/23-24/86	2330-0730	890	1200	640	320
10/25/86	1000-1700	130	170	49	21

Table IV-4D. Particulate Mutagen Densities, Yuba City, October 1986

Date	Time of Day (PDT)	Mutagen Density (rev m^{-3})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP$_6$ -S9
10/16/86	0700-1900	17	24	10	3.5
10/16-17/86	1900-0700	2.8	4.3	2.7	1.5
10/17/86	0700-1700	25	24	12	4.9
10/18/86	0700-1900	10	7.8	4.2	1.4
10/18-19/86	1900-0700	7.6	6.2	2.6	1.8
10/20/86	0900-1900	15	11	3.9	2.1
10/20-21/86	1900-0700	36	36	22	9.0
10/21/86	0700-1900	28	46	23	9.4
10/21-22/86	1900-0700	39	60	32	14
10/23/86	0830-1620	82	95	50	19
10/23-24/86	2330-0730	41	57	29	15
10/25/86	1000-1700	5.6	7.4	2.2	0.93

[a]Average flow rates for the two samplers were 40.4 SCFM (Hi-vol #8) and 38.7 SCFM (Hi-vol #11) for a total sampling volume of 1612 m^3.

Table IV-5A. Sampling Data for Particulate Collections at Concord, December 1986 and January 1987

Date	Time of Day (PST)	Particulate Weight; 2 Filters (mg)	Sampling Volume (m^3)	TSP ($\mu g\ m^{-3}$)	Extract Weight (mg)	% Extractable[a]
12/6-7/86	2030-0500	77.0	1227.5	63	63.47	82
12/7/86	0500-1700	19.7	1732.9	11	10.47	53
12/7-8/86	1700-0500	110.2	1732.9	64	96.22	87
12/8/86	0500-1700	73.2	1732.9	42	42.65	58
12/8-9/86	1700-0500	151.0	1732.9	87	112.72	75
12/9/86	0500-1700	87.1	1732.9	50	52.30	60
12/10-11/86	1700-0500	106.6	1732.9	62	51.66	48
12/12/86	0500-1700	86.2	1732.9	50	49.28	57
1/13/87	0900-1700	15.1	1155.3	13	7.07	47
1/13-14/86	1815-0500	55.0	1552.4	35	32.80	60
1/14/87	0500-1700	44.8	1732.9	26	20.70	46
1/14-15/87	1700-0500	46.8	1732.9	27	24.26	52
1/17-18/87	1700-0500	198.1	1732.9	114	156.78	79
1/18/87	0500-1700	153.8	1732.9	89	124.45	81
1/18-19/87	1700-0500	178.0	1732.9	103	124.67	70
1/19/87	0500-1422	87.3	1352.6	65	48.41	55
1/21/87	0500-1700	135.4	1732.9	78	100.57	74
1/21-22/87	1700-0500	210.6	1732.9	122	140.48	67
1/22/87	0500-1600	172.6	1588.5	109	124.12	72

[a]16-hr Soxhlet extraction with benzene/methanol (80/20).

Table IV-5B. Specific Activities of Particulate Extracts Collected at Concord, December 1986 and January 1987

Date	Time of Day (PST)	Specific Activity (rev μg^{-1})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9	Ratios of Response (-S9) TA98NR to TA98	TA98/ 1,8-DNP_6 to TA98
12/6-7/86	2030-0500	1.1 (13)	1.0 (7.4)	0.55 (5.0)	0.20 (6.9)	0.55	0.20
12/7/86	0500-1700	1.4 (4.9)	1.4 (8.5)	0.56 (5.1)	0.26 (8.2)	0.40	0.19
12/7-8/86	1700-0500	0.98 (3.1)	0.71 (7.7)	0.43 (12)	0.20 (7.6)	0.61	0.28
12/8/86	0500-1700	2.3 (3.1)	2.9 (4.3)	1.4 (5.6)	0.60 (7.4)	0.48	0.21
12/8-9/86	1700-0500	1.1 (5.0)	1.1 (3.8)	0.58 (3.3)	0.42 (3.1)	0.53	0.38
12/9/86	0500-1700	1.7 (4.6)	2.0 (1.2)	1.2 (3.2)	0.54 (4.6)	0.60	0.27
12/10-11/86	1700-0500	2.2 (2.4)	3.0 (3.0)	1.4 (5.1)	0.88 (6.8)	0.47	0.29
12/12/86	0500-1700	0.71 (5.3)	0.86 (4.0)	0.36 (2.9)	0.15 (9.6)	0.42	0.17
1/13/87	0900-1700	1.7 (5.0)	2.0 (9.4)	0.81 (2.2)	0.31 (5.1)	0.41	0.16
1/13-14/87	1815-0500	1.1 (6.5)	0.58 (4.5)	0.49 (4.5)	0.18 (8.3)	0.84	0.31
1/14/87	0500-1700	4.5 (3.7)	5.0 (3.3)	2.9 (2.2)	1.3 (9.2)	0.58	0.26
1/14-15/897	1700-0500	2.6 (1.7)	3.2 (3.9)	1.5 (3.2)	0.75 (6.3)	0.47	0.23
1/17-18/87	1700-0500	1.2 (2.2)	0.71 (5.0)	0.48 (5.0)	0.28 (11)	0.68	0.39
1/18/87	0500-1700	1.2 (3.0)	1.2 (3.6)	0.51 (2.6)	0.21 (4.9)	0.43	0.18
1/18-19/87	1700-0500	0.86 (2.2)	0.78 (4.0)	0.38 (4.9)	0.17 (10)	0.49	0.22
1/19/87	0500-1422	3.0 (2.8)	3.7 (1.7)	1.6 (3.5)	1.0 (2.8)	0.43	0.27
1/21/87	0500-1700	0.99 (3.3)	1.2 (1.7)	0.59 (2.9)	0.28 (9.4)	0.49	0.23
1/21-22/87	1700-0500	1.7 (3.6)	1.2 (3.5)	0.84 (5.3)	0.41 (5.2)	0.70	0.34
1/22/87	0500-1600	1.5 (3.6)	1.7 (2.7)	0.75 (2.4)	0.33 (3.8)	0.44	0.19

[a]Slope of the dose-response curve in the region of linear response. The number in parentheses is the standard error expressed as a percentage of the specific activity.

Table IV-5C. Mutagen Loadings of Particulate Matter Collected at Concord, December 1986 and January 1987

Date	Time of Day (PST)	Mutagen Loading (rev mg^{-1})			
		TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
12/6-7/86	2030-0500	910	820	450	160
12/7/86	0500-1700	740	740	300	140
12/7-8/86	1700-0500	860	620	380	170
12/8/86	0500-1700	1300	1700	820	350
12/8-9/86	1700-0500	820	820	430	310
12/9/86	0500-1700	1000	1200	720	320
12/10-11/86	1700-0500	1100	1500	680	430
12/12/86	0500-1700	410	490	210	86
1/13/87	0900-1700	800	940	380	150
1/13-14/87	1815-0500	660	350	290	110
1/14/87	0500-1700	2100	2300	1300	600
1/14-15/87	1700-0500	1300	1700	780	390
1/17-18/87	1700-0500	950	560	380	220
1/18/87	0500-1700	970	970	410	170
1/18-19/87	1700-0500	600	550	270	120
1/19/87	0500-1422	1700	2100	890	550
1/21/87	0500-1700	740	890	440	210
1/21-22/87	1700-0500	1100	800	560	270
1/22/87	0500-1600	1100	1200	540	240

Table IV-5D. Particulate Mutagen Densities, Concord, December 1986 and January 1987

Date	Time of Day (PST)	Mutagen Density (rev m^{-3}) TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
12/6-7/86	2030-0500	57	52	28	10
12/7/86	0500-1700	8.5	8.5	3.4	1.6
12/7-8/86	1700-0500	54	39	24	11
12/8/86	0500-1700	57	71	34	15
12/8-9/86	1700-0500	72	72	38	27
12/9/86	0500-1700	51	60	36	16
12/10-11/86	1700-0500	66	89	42	26
12/12/86	0500-1700	20	24	10	4.3
1/13/87	0900-1700	10	12	5.0	1.9
1/13-14/87	1815-0500	23	12	10	3.8
1/14/87	0500-1700	54	60	35	16
1/14-15/87	1700-0500	36	45	21	10
1/17-18/87	1700-0500	110	64	43	25
1/18/87	0500-1700	86	86	37	15
1/18-19/87	1700-0500	62	56	27	12
1/19/87	0500-1422	110	130	57	36
1/21/87	0500-1700	57	70	34	16
1/21-22/87	1700-0500	140	97	68	33
1/22/87	0500-1600	120	130	59	26

Table IV-6A. Sampling Data for Particulate Collections at Mammoth Lakes, February and March 1987

Date	Time of Day (PST)	Particulate Weight; 2 Filters (mg)	Sampling Volume (m^3)	TSP ($\mu g\ m^{-3}$)	Extract Weight (mg)	% Extractable[a]
2/14/87	0500-1700	49.4	1233.4	40	37.43	76
2/14/87	1700-2330	31.6	668.1	47	17.32	55
2/15-16/87	1730-0500	85.7	1182.0	73	75.25	88
2/16/87	0500-1700	36.4	1233.4	30	18.02	50
2/16-17/87	1700-0500	148.2	1233.4	120	128.57	87
2/17/87	0500-1700	16.7	1233.4	14	8.51	51
2/17-18/87	1700-0500	98.6	1233.4	80	91.00	92
2/20-21/87	1700-0500	133.5	1333.3	100	118.60	89
2/21/87	0500-1700	48.5	1333.3	36	20.56	42
2/21-22/87	1700-0500	49.6	1284.4	39	20.38	41
2/22/87	0500-1700	47.3	1284.4	37	19.53	41
2/22-23/87	1700-0500	37.0	1284.4	29	10.40	28
2/25-26/87	1700-0500	33.1	1284.4	26	26.50	80
2/26/87	0500-1700	23.8	1284.4	19	17.84	75
2/27-28/87	1700-0500	176.6	1284.4	140	171.45	97
2/28/87	0500-1700	52.4	1284.4	41	4.21	8.0
2/28-3/1/87	1700-0500	171.6	1284.4	130	147.61	86

[a]16-hr Soxhlet extraction with benzene/methanol (80/20).

Table IV-6B. Specific Activities of Particulate Extracts Collected at Mammoth Lakes, February and March 1987

Date	Time of Day (PST)	Specific Activity (rev μg^{-1})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9	Ratios of Response (-S9) TA98NR to TA98	TA98/ 1,8-DNP_6 to TA98
2/14/87	0500-1700	0.73 (13)	0.34 (3.0)	0.13 (7.2)	0.13 (11)	0.38	0.38
2/14/87	1700-2330	0.55 (7.0)	0.20 (8.1)	0.084 (10)	0.043 (9.8)	0.42	0.22
2/15-16/87	1730-0500	0.24 (38)	0.13 (6.3)	0.064 (10)	0.027 (26)	0.49	0.21
2/16/87	0500-1700	0.71 (23)	0.14 (10)	0.090 (13)	0.049 (6.3)	0.64	0.35
2/16-17/87	1700-0500	0.43 (21)	0.094 (11)	0.068 (11)	0.022 (19)	0.72	0.23
2/17/87	0500-1700	0.57 (6.6)	0.20 (10)	0.11 (11)	0.038 (28)	0.55	0.19
2/17-18/87	1700-0500	0.27 (9.4)	0.13 (11)	0.090 (9.2)	0.024 (22)	0.69	0.18
2/20-21/87	1700-0500	0.94 (22)	0.17 (6.2)	0.14 (7.1)	0.014 (39)	0.82	0.082
2/21/87	0500-1700	0.77 (7.6)	0.54 (6.7)	0.17 (9.5)	0.11 (10)	0.31	0.20
2/21-22/87	1700-0500	0.64 (9.9)	0.11 (15)	0.11 (2.8)	0.017 (31)	1.0	0.15
2/22/87	0500-1700	1.5 (4.3)	1.1 (4.1)	0.58 (2.4)	0.27 (8.5)	0.53	0.25
2/22-23/87	1700-0500	0.75 (6.2)	0.62 (3.1)	0.25 (5.3)	0.11 (12)	0.40	0.18
2/25-26/87	1700-0500	0.17 (18)	0.089 (17)	0.046 (8.5)	0.016 (27)	0.52	0.18
2/26/87	0500-1700	0.82 (16)	0.21 (7.2)	0.11 (13)	0.088 (12)	0.52	0.42
2/27-28/87	1700-0500	0.31 (28)	0.061 (16)	0.052 (12)	0.005 (22)	0.85	0.08
2/28/87	0500-1700	1.3 (4.4)	0.42 (9.6)	0.24 (9.5)	0.12 (18)	0.57	0.29
2/28-3/1/87	1700-0500	0.46 (18)	0.11 (10)	0.076 (14)	0.027 (8.6)	0.69	0.25

[a]Slope of the dose-response curve in the region of linear response. The number in parentheses is the standard error expressed as a percentage of the specific activity.

Table IV-6C. Mutagen Loadings of Particulate Matter Collected at Mammoth Lakes, February and March 1987

Date	Time of Day (PST)	Mutagen Loading (rev mg^{-1})			
		TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
2/14/87	0500-1700	550	260	99	99
2/14/87	1700-2330	300	110	46	24
2/15-16/87	1730-0500	210	110	56	24
2/16/87	0500-1700	350	69	45	24
2/16-17/87	1700-0500	370	82	59	19
2/17/87	0500-1700	290	100	56	19
2/17-18/87	1700-0500	250	120	83	22
2/20-21/87	1700-0500	840	150	120	12
2/21/87	0500-1700	330	230	72	47
2/21-22/87	1700-0500	260	45	45	7.0
2/22/87	0500-1700	620	450	240	110
2/22-23/87	1700-0500	210	170	70	31
2/25-26/87	1700-0500	140	71	37	13
2/26/87	0500-1700	610	160	82	66
2/27-28/87	1700-0500	300	59	50	5
2/28/87	0500-1700	100	34	19	10
2/28-3/1/87	1700-0500	400	95	65	23

Table IV-6D. Particulate Mutagen Densities, Mammoth Lakes, February and March 1987

Date	Time of Day (PST)	Mutagen Density (rev m^{-3}) TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
2/14/87	0500-1700	22	10	3.9	3.9
2/14/87	1700-2330	14	5.2	2.2	1.1
2/15-16/87	1730-0500	15	8.3	4.1	1.7
2/16/87	0500-1700	10	2.0	1.3	0.72
2/16-17/87	1700-0500	45	9.8	7.1	2.3
2/17/87	0500-1700	3.9	1.4	0.76	0.26
2/17-18/87	1700-0500	20	9.6	6.6	1.8
2/20-21/87	1700-0500	84	15	12	1.2
2/21/87	0500-1700	12	8.3	2.6	1.7
2/21-22/87	1700-0500	10	1.7	1.7	0.27
2/22/87	0500-1700	23	17	8.8	4.1
2/22-23/87	1700-0500	6.1	5.0	2.0	0.89
2/25-26/87	1700-0500	3.5	1.8	0.95	0.33
2/26/87	0500-1700	11	2.9	1.5	1.2
2/27-28/87	1700-0500	41	8.1	6.9	0.67
2/28/87	0500-1700	4.3	1.4	0.79	0.39
2/28-3/1/87	1700-0500	53	13	8.7	3.1

Table IV-7A. Sampling Data for Particulate Collections at Oildale, March and April 1987

Date	Time of Day[a]	Particulate Weight; 2 Filters (mg)	Sampling Volume (m^3)	TSP ($\mu g\ m^{-3}$)	Extract Weight (mg)	% Extractable[b]
3/29-30/87	1800-0600	35.2	1602.4	22	6.34	18
3/30/87	0600-1800	52.5	1602.4	33	7.89	15
3/31/87	0745-1800	59.8	1368.8	44	9.15	15
3/31-4/1/87	1800-0600	75.2	1602.4	47	19.66	26
4/1/87	0600-1800	77.8	1602.4	49	17.20	22
4/1-2/87	1800-0600	73.5	1602.4	46	10.13	14
4/2/87	0600-1800	67.8	1602.4	42	18.84	28
4/7/87	0700-1900	64.1	1602.4	40	20.60	32
4/7-8/87	1900-0700	117.7	1602.4	73	18.10	15
4/8/87	0700-1900	66.8	1602.4	42	16.27	24
4/8-9/87	1900-0700	94.6	1602.4	59	21.06	22
4/9/87	0700-1900	68.6	1602.4	43	14.26	21
4/9-10/87	1900-0700	93.0	1602.4	58	27.78	30
4/10/87	0700-1900	79.5	1602.4	50	17.14	22
4/10-11/87	1900-0700	72.6	1602.4	45	16.72	23

[a]Times are PST for 3/29/87 through 4/2/87; PDT for 4/7/87 through 4/11/87.
[b]16-hr Soxhlet extraction with benzene/methanol (80/20).

Table IV-7B. Specific Activities of Particulate Extracts Collected at Oildale, March and April 1987

Date	Time of Day[b]	Specific Activity (rev μg^{-1})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9	Ratios of Response (-S9) TA98NR to TA98	TA98/ 1,8-DNP_6 to TA98
3/29-30/87	1800-0600	1.2 (7.4)	0.93 (3.8)	0.52 (3.8)	0.34 (5.2)	0.56	0.37
3/30/87	0600-1800	1.6 (3.6)	1.1 (3.7)	0.59 (9.7)	0.23 (9.1)	0.54	0.21
3/31/87	0745-1800	1.7 (4.0)	1.2 (6.7)	0.46 (7.8)	0.20 (11)	0.38	0.17
3/31-4/1/87	1800-0600	1.1 (4.5)	1.1 (1.6)	0.60 (3.1)	0.28 (2.8)	0.55	0.25
4/1/87	0600-1800	0.65 (2.2)	0.65 (5.5)	0.24 (5.0)	0.16 (5.0)	0.37	0.25
4/1-2/87	1800-0600	1.4 (2.4)	1.3 (2.9)	0.40 (6.1)	0.15 (11)	0.31	0.12
4/2/87	0600-1800	0.61 (3.4)	0.65 (3.5)	0.20 (8.0)	0.13 (8.7)	0.31	0.20
4/7/87	0700-1900	0.54 (1.7)	0.53 (3.9)	0.23 (3.8)	0.079 (16)	0.43	0.15
4/7-8/87	1900-0700	2.0 (4.4)	1.8 (2.6)	0.76 (3.7)	0.33 (6.1)	0.42	0.18
4/8/87	0700-1900	0.71 (6.6)	0.65 (3.6)	0.19 (4.9)	0.11 (14)	0.29	0.17
4/8-9/87	1900-0700	1.9 (2.6)	1.3 (2.5)	0.56 (3.5)	0.22 (6.5)	0.43	0.17
4/9/87	0700-1900	0.96 (5.1)	0.78 (2.5)	0.24 (2.6)	0.085 (20)	0.31	0.11
4/9-10/87	1900-0700	0.72 (4.5)	0.72 (3.7)	0.42 (3.0)	0.19 (6.7)	0.58	0.26
4/10/87	0700-1900	0.55 (7.1)	0.59 (3.5)	0.18 (6.9)	0.091 (9.0)	0.31	0.15
4/10-11/87	1900-0700	0.44 (6.2)	0.39 (5.2)	0.20 (8.1)	0.072 (14)	0.51	0.18

[a]Slope of the dose-response curve in the region of linear response. The number in parentheses is the standard error expressed as a percentage of the specific activity.
[b]Times are PST for 3/29/87 through 4/2/87; PDT for 4/7/87 through 4/11/87.

Table IV-7C. Mutagen Loadings of Particulate Matter Collected at Oildale, March and April 1987

Date	Time of Day[a]	Mutagen Loading (rev mg^{-1}) TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
3/29-30/87	1800-0600	220	170	94	61
3/30/87	0600-1800	240	170	89	35
3/31/87	0745-1800	260	180	70	31
3/31-4/1/87	1800-0600	290	290	160	73
4/1/87	0600-1800	140	140	53	35
4/1-2/87	1800-0600	190	180	55	21
4/2/87	0600-1800	170	180	56	36
4/7/87	0700-1900	170	170	74	25
4/7-8/87	1900-0700	310	280	120	51
4/8/87	0700-1900	170	160	46	27
4/8-9/87	1900-0700	420	290	120	49
4/9/87	0700-1900	200	160	50	18
4/9-10/87	1900-0700	220	220	130	57
4/10/87	0700-1900	120	130	39	20
4/10-11/87	1900-0700	100	90	46	17

[a]Times are PST for 3/2/87 through 4/2/87; PDT for 4/7/87 through 4/11/87.

Table IV-7D. Particulate Mutagen Densities, Oildale, March and April 1987

Date	Time of Day[a]	Mutagen Density (rev m^{-3}) TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
3/29-30/87	1800-0600	4.7	3.7	2.1	1.3
3/30/87	0600-1800	7.9	5.4	2.9	1.1
3/31/87	0745-1800	11	8.0	3.1	1.3
3/31-4/1/87	1800-0600	13	13	7.4	3.4
4/1/87	0600-1800	7.0	7.0	2.6	1.7
4/1-2/87	1800-0600	8.9	8.2	2.5	0.95
4/2/87	0600-1800	7.2	7.6	2.4	1.5
4/7/87	0700-1900	6.9	6.8	3.0	1.0
4/7-8/87	1900-0700	23	20	8.6	3.7
4/8/87	0700-1900	7.2	6.6	1.9	1.1
4/8-9/87	1900-0700	25	17	7.4	2.9
4/9/87	0700-1900	8.5	6.9	2.1	0.76
4/9-10/87	1900-0700	12	12	7.3	3.3
4/10/87	0700-1900	5.9	6.3	1.9	1.0
4/10-11/87	1900-0700	4.6	4.1	2.1	0.75

[a]Times are PST for 3/29/87 through 4/2/87; PDT for 4/7/87 through 4/11/87.

Table IV-8A. Sampling Data for Particulate Collections at Reseda, May and June 1987

Date	Time of Day (PDT)	Particulate Weight; 2 Filters (mg)	Sampling Volume (m^3)	TSP ($\mu g\ m^{-3}$)	Extract Weight (mg)	% Extractable[a]
5/27-28/87	2000-0700	54.4	1496.9	36	25.22	46
5/28/87	0700-1900	63.3	1633.0	39	17.44	28
5/28-29/87	1900-0700	56.9	1633.0	35	23.68	42
5/29/87	0700-1900	85.2	1633.0	52	32.25	38
5/29-30/87	1900-0700	68.2	1633.0	42	32.65	48
5/30/87	0700-1900	75.0	1633.0	46	26.05	35
5/30-31/87	1900-0700	87.4	1633.0	54	37.20	43
5/31/87	0700-1900	77.8	1633.0	48	28.27	36
5/31-6/1/87	1900-0700	85.0	1633.0	52	35.71	42
6/1/87	0700-1900	71.8	1633.0	44	27.61	38
6/1-2/87	1900-0700	86.9	1633.0	53	22.18	26
6/2/87	0700-1900	93.4	1633.0	57	35.50	38
6/2-3/87	1900-0700	102.0	1633.0	62	62.04	61
6/13-14/87	1900-0700	117.6	1633.0	72	49.72	42
6/14/87	0700-1900	67.4	1633.0	41	20.52	30
6/14-15/87	1900-0700	33.0	1633.0	20	13.59	41
6/15/87	0700-1900	47.2	1633.0	29	12.38	26

[a]16-hr Soxhlet extraction with benzene/methanol (80/20).

Table IV-8B. Specific Activities of Particulate Extracts Collected at Reseda, May and June 1987

Date	Time of Day (PDT)	Specific Activity (rev μg^{-1})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9	Ratios of Response (-S9) TA98NR to TA98	TA98/ 1,8-DNP_6 to TA98
5/27-28/87	2000-0700	1.3 (4.3)	1.5 (2.4)	0.86 (4.5)	0.43 (3.6)	0.57	0.29
5/28/87	0700-1900	1.6 (3.0)	2.1 (3.1)	0.74 (2.8)	0.38 (4.9)	0.35	0.18
5/28-29/87	1900-0700	1.4 (4.4)	1.4 (4.1)	0.78 (4.2)	0.40 (4.6)	0.56	0.29
5/29/87	0700-1900	0.98 (4.8)	1.1 (3.4)	0.39 (4.4)	0.17 (7.4)	0.35	0.15
5/29-30/87	1900-0700	1.1 (2.1)	1.4 (1.8)	0.65 (2.5)	0.41 (2.9)	0.46	0.29
5/30/87	0700-1800	0.87 (5.6)	0.94 (3.0)	0.33 (3.0)	0.18 (6.8)	0.35	0.19
5/30-31/87	1900-0700	1.5 (7.0)	1.5 (3.2)	0.71 (1.6)	0.41 (2.9)	0.47	0.27
5/31/87	0700-1900	0.79 (5.3)	0.99 (3.3)	0.31 (4.8)	0.16 (3.1)	0.31	0.16
5/31-6/1/87	1900-0700	1.8 (3.8)	2.3 (0.8)	0.89 (2.9)	0.57 (2.4)	0.39	0.25
6/1/87	0700-1900	1.3 (3.9)	1.4 (6.3)	0.49 (4.6)	0.20 (4.2)	0.35	0.14
6/1-2/87	1900-0700	0.90 (5.8)	1.1 (6.4)	0.37 (2.6)	0.25 (7.6)	0.34	0.23
6/2/87	0700-1900	1.2 (5.2)	1.4 (2.9)	0.46 (1.2)	0.20 (3.3)	0.33	0.14
6/2-3/87	1900-0700	0.40 (4.5)	0.66 (2.8)	0.32 (2.8)	0.18 (3.3)	0.48	0.27
6/13-14/87	1900-0700	0.66 (7.4)	0.85 (3.1)	0.36 (2.1)	0.18 (4.0)	0.42	0.21
6/14/87	0700-1900	0.52 (6.9)	0.73 (3.5)	0.26 (9.3)	0.14 (4.9)	0.36	0.19
6/14-15/87	1900-0700	0.82 (3.9)	0.89 (2.4)	0.45 (2.4)	0.32 (5.4)	0.51	0.36
6/15/87	0700-1900	0.89 (6.9)	0.67 (7.6)	0.18 (11)	0.096 (8.2)	0.27	0.14

[a]Slope of the dose-response curve in the region of linear response. The number in parentheses is the standard error expressed as a percentage of the specific activity.

Table IV-8C. Mutagen Loadings of Particulate Matter Collected at Reseda, May and June 1987

Date	Time of Day (PDT)	Mutagen Loading (rev mg^{-1}) TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
5/27-28/87	2000-0700	600	700	400	200
5/28/87	0700-1900	440	580	200	100
5/28-29/87	1900-0700	580	580	320	170
5/29/87	0700-1900	370	420	150	64
5/29-30/87	1900-0700	530	670	310	200
5/30/87	0700-1800	300	330	110	63
5/30-31/87	1900-0700	640	640	300	170
5/31/87	0700-1900	290	360	110	58
5/31-6/1/87	1900-0700	760	970	370	240
6/1/87	0700-1900	500	540	190	77
6/1-2/87	1900-0700	230	280	94	64
6/2/87	0700-1900	460	530	170	76
6/2-3/87	1900-0700	240	400	190	110
6/13-14/87	1900-0700	280	360	150	76
6/14/87	0700-1900	160	220	79	43
6/14-15/87	1900-0700	340	370	190	130
6/15/87	0700-1900	230	180	47	25

Table IV-8D. Particulate Mutagen Densities, Reseda, May and June 1987

Date	Time of Day (PDT)	Mutagen Density (rev m^{-3}) TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
5/27-28/87	2000-0700	22	25	14	7.2
5/28/87	0700-1900	17	22	7.9	4.1
5/28-29/87	1900-0700	20	20	11	5.8
5/29/87	0700-1900	19	22	7.7	3.4
5/29-30/87	1900-0700	22	28	13	8.2
5/30/87	0700-1800	14	15	5.3	2.9
5/30-31/87	1900-0700	34	34	16	9.3
5/31/87	0700-1900	14	17	5.4	2.8
5/31-6/1/87	1900-0700	39	50	19	12
6/1/87	0700-1900	22	24	8.3	3.4
6/1-2/87	1900-0700	12	15	5.0	3.4
6/2/87	0700-1900	26	30	10	4.3
6/2-3/87	1900-0700	15	25	12	6.8
6/13-14/87	1900-0700	20	26	11	5.5
6/14/87	0700-1900	6.5	9.2	3.3	1.8
6/14-15/87	1900-0700	6.8	7.4	3.7	2.7
6/15/87	0700-1900	6.7	5.1	1.4	0.73

Table IV-9A. Sampling Data for Particulate Collections at Pt. Arguello, Vandenberg AFB, July 1987

Dates	Time of Day (PDT)	Particulate Weight (mg)	Sampling Volume (m^3)	TSP ($\mu g\ m^{-3}$)	Extract Weight (mg)	% Extractable[a]
7/4, 7/5, 7/6 7/7, 7/8/87	0700-1900	493.9[b]	8,043	61	189.07	38
7/4-5, 7/5-6, 7/6-7, 7/7-8, 7/8-9/87	1900-0700[c]	620.6[b]	7,808	79	216.95	35
7/9, 7/10, 7/11, 7/12, 7/13/87	0700-1900	479.5[d]	7,238	66	124.64	26
7/9-10, 7/10-11, 7/11-12, 7/12-13, 7/13-14/87	1900-0700	318.6[b]	8,043	40	68.72	22

[a]16-hr Soxhlet extraction with benzene/methanol (80/20).
[b]10 filters.
[c]Except 7/7-8/87 which was 2045-0700 hr.
[d]9 Filters.

Table IV-9B. Specific Activities of Particulate Extracts Collected at Pt. Arguello, Vandenberg AFB, July 1987

Dates	Time of Day (PDT)	Specific Activity (rev μg^{-1})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9	Ratios of Response (-S9) TA98NR to TA98	TA98/ 1,8-DNP_6 to TA98
7/4, 7/5, 7/6 7/7, 7/8/87	0700-1900	0.0047[b] (67)	0.013 (25)	0.0070 (18)	0.0042 (29)	0.54	0.32
7/4-5, 7/5-6, 7/6-7, 7/7-8, 7/8-9/87	1900-0700[c]	0.0099 (17)	0.015 (17)	0.0072 (8.9)	0.0047 (23)	0.48	0.31
7/9, 7/10, 7/11, 7/12, 7/13/87	0700-1900	0.019 (16)	0.031 (13)	0.011 (10)	0.0078 (32)	0.35	0.25
7/9-10, 7/10-11, 7/11-12, 7/12-13, 7/13-14/87	1900-0700	0.020 (31)	0.046 (18)	0.025 (14)	0.017 (13)	0.54	0.37

[a]Slope of the dose-response curve in the region of linear response. The number in parentheses is the standard error expressed as a percentage of the specific activity.
[b]Slope of dose-response curve significant at the 80% confidence level only. All other specific activities are significant at the 95% confidence level.
[c]Except 7/7-8/87 which was 2045-0700 hr.

Table IV-9C. Mutagen Loadings of Particulate Matter Collected at Pt. Arguello, Vandenberg AFB, July 1987

Dates	Time of Day (PDT)	Mutagen Loading (rev mg^{-1}) TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
7/4, 7/5, 7/6, 7/7, 7/8/87	0700-1900	1.8[a]	5.0	2.7	1.6
7/4-5, 7/5-6, 7/6-7, 7/7-8, 7/8-9/87	1900-0700[b]	3.5	5.2	2.5	1.6
7/9, 7/10, 7/11, 7/12, 7/13/87	0700-1900	4.9	8.1	2.9	2.0
7/9-10, 7/10-11, 7/11-12, 7/12-13, 7/13-14/87	1900-0700	4.3	9.9	5.4	3.7

[a]Specific activity significant at 80% confidence only.
[b]Except 7/7-8/87 which was 2045-0700 hr.

Table IV-9D. Particulate Mutagen Densities, Pt. Arguello, Vandenberg AFB, July 1987

Dates	Time of Day (PDT)	Mutagen Density (rev m^{-3}) TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
7/4, 7/5, 7/6, 7/7, 7/8/87	0700-1900	0.11[a]	0.31	0.16	0.10
7/4-5, 7/5-6, 7/6-7, 7/7-8, 7/8-9/87	1900-0700[b]	0.28	0.42	0.20	0.13
7/9, 7/10, 7/11, 7/12, 7/13/87	0700-1900	0.33	0.53	0.19	0.13
7/9-10, 7/10-11, 7/11-12, 7/12-13, 7/13-14/87	1900-0700	0.17	0.39	0.21	0.15

[a]Specific activity significant at 80% confidence only.
[b]Except 7/7-8/87 which was 2045-0700 hr.

suspended particulate [TSP] and percent extractable data), (B) specific activities (extract potencies), (C) mutagen loadings (particulate potencies) and (D) mutagen density (airborne mutagenicity concentrations).

At Glendora, the final nighttime sampling period (8/20-21/86; 2000-0800 PDT) was unusual because of the high levels of volatile and non-volatile nitroarenes present in the atmosphere. For example, the 2-nitrofluoranthene concentration was a factor of ~5 greater than on the previous day and the 1-nitronaphthalene concentration increased by over a factor of two (see Section VII). Concurrent observations of the presence of the nitrate radical indicated that N_2O_5 chemistry could have been occurring on this night (see Table V-2 and Final Report to ARB Contract No. A5-150-32). Our measured mutagen density, however, declined by a factor of two, inconsistent with these other observations. Moreover, in contrast to our results, researchers at General Motors Laboratories using CH_2Cl_2 as an extraction solvent observed a significant increase in mutagenicity (TA98, -S9) from the daytime (8/20/86; 0800-2000 PDT) sample to the nighttime (8/20-21/86; 2000-0800 PDT) sample in their tests. Since we had used a benzene-methanol azeotrope as the extraction solvent system, we retested the POM collected during these final two sampling periods using dichloromethane as the extraction solvent.

For this second mutagenicity test using CH_2Cl_2-extraction, the TIGF filters from the Hi-vol samplers with PUF plugs were employed. As noted in Section III, these modified Hi-vol samplers were operated at a reduced flow rate (23 SCFM at Glendora) and were not equipped with inlets. One filter from the daytime (8/20/86; 0800-2000 PDT) and one filter from the nighttime (8/20-21/86; 2000-0800 PDT) collection period were Soxhlet extracted for 16 hours with CH_2Cl_2, and tested on TA98 (-S9).

The results of this collection and mutagenicity test are given in Table IV-10, together with the data for our previous test of the benzene-methanol extracts. As can be seen from the TSP data, the modified samplers collected more particulate matter than the standard Hi-vol, as expected since these Hi-vols were not equipped with a size-selective inlet. This was not expected to have greatly affected the mutagenicity results, however, because very little mutagenicity is associated with particles larger than ~10 μm (Talcott and Harger 1980).

Table IV-10. The Effect of Extraction Solvent on Mutagenicity (TA98, -S9) at Glendora

	Benzene-Methanol Extracts		CH_2Cl_2 Extracts	
Date	8/20/86	8/20-21/86	8/20/86	8/20-21/86
Time Period (PDT)	Day 0800-2000	Night 2000-0800	Day 0800-2000	Night 2000-0800
Flow Rate (SCFM)	40.0	40.0	23.0	23.0
TSP ($\mu g\ m^{-3}$)	120	72	160	110
% Extractable	26	24	12	14
Specific Activity (rev μg^{-1})	2.0	1.6	2.5	5.5
Mutagen Loading (rev mg^{-1})	530	390	300	760
Mutagen Density (rev m^{-3})	61	28	47	83

The more polar benzene-methanol solvent system extracted much more material than did CH_2Cl_2. Despite the larger amount of polar material present in the benzene-methanol samples, the mutagen density for the nighttime sample is three-fold lower than for the corresponding CH_2Cl_2-extracted sample. In contrast, the mutagen density for the benzene-methanol daytime sample is somewhat higher than for the corresponding CH_2Cl_2-extracted sample. Apparently, the polar material in the benzene-methanol extract of the nighttime sample inhibited the mutagenicity of this extract, probably through toxic or bacteriostatic action. In contrast, the mutagenicity of the polar compounds in the daytime sample overcame any inhibitory effect.

These observations illustrate the inherent compromises in choosing a solvent system for extracting ambient particles. We chose the benzene-methanol solvent system precisely because it extracts more polar material than does CH_2Cl_2 and does not generate the artifactual mutagenicity

associated with the use of acetonitrile (Winer et al. 1987). Indeed, because inhibitory compounds may be of the same polarity as mutagens, every solvent system must result in an underestimation of the mutagenicity of ambient POM. This underscores the need for identification and quantification of ambient mutagens. Once identified and tested for mutagenicity in their pure form, the known mutagens in a sample can be quantified and an accurate sum of their mutagenicities can be obtained.

The overall mutagenicity results obtained in this study are summarized in Table IV-11, which lists average and maximum mutagen densities observed at each site. In general, the observed mutagenicity was essentially unchanged in the presence of S9, indicating a dominant effect of direct-acting mutagenicity. The notable exception was the Mammoth Lakes site where high wood-burning emissions, rich in PAH, are reflected in a dominance of promutagenicity over direct activity. Not surprisingly the rural site, Pt. Arguello, has an average mutagen density an order of magnitude lower than the other sites. Interestingly, the highest average mutagen density was observed at the industrial site in Concord. Correlations of these mutagenicity data with ambient PAH and PAH-derivative concentrations are explored and discussed in Section X.

Table IV-11. Summary of Mutagenicity Observed in California 1986-1987

		Average Mutagen Density (rev m^{-3}) TA98		Highest Value
		+S9	-S9	(-S9)
8/86	Glendora	33	35 (37)[a]	61
10/86	Yuba City	24	30	95
12/86-1/87	Concord	63	62	130
2-3/87	Mammoth Lakes	22	7	17 (84 with S9)
3-4/87	Oildale	10	9	20
5-6/87	Reseda	19	22	50
7/87	Pt. Arguello	0.2	0.4	0.5

[a]Using the mutagenicity data from dichloromethane extracts of the 0800-2000 PDT 8/20/86 and 2000-0800 PDT, 8/20-21/86 samples.

V. COMPOSITING OF PUF AND FILTER SAMPLES FOR CHEMICAL ANALYSIS

As discussed above in Section III, ambient air samples were collected onto Tenax-GC solid adsorbent, PUF plugs and TIGF filters at the seven sites specifically involved in this study (Glendora, Yuba City, Concord, Mammoth Lakes, Oildale, Reseda and Pt. Arguello). In addition, particulate matter was collected at San Nicolas Island during the South Coast Air Quality Study on TIGF filters on a 0100 hr/1300 hr time schedule. As described above in Section IV, for the ambient air samples collected at Glendora, Yuba City, Concord, Mammoth Lakes, Oildale and Reseda, two of the TIGF filters from the Hi-vol samplers equipped with inlets were composited for each of the 12-hr sample time periods and these two-filter composites were analyzed for mutagenicity. For the Pt. Arguello site, due to the low levels of ambient mutagenicity observed in a preliminary test, the two TIGF filters from each 12-hr ambient air collection period designated for mutagenicity analysis were composited into only two nighttime and two daytime samples prior to mutagenicity testing (Section IV). The low flow (~1 L min^{-1}) Tenax-GC solid adsorbent samples were analyzed for naphthalene for each of the individual 12-hr sample time periods, thus providing the same 12-hr "time-resolution" as the mutagenicity data.

However, it was anticipated that speciated PAH and PAH-derivative chemical analyses would not be possible for the PUF plug and TIGF filter samples from each 12-hr collection period due to the small amounts of sample available. Thus, it was necessary to combine, or composite, individual 12-hr PUF plug and TIGF filter samples for chemical analyses. To allow for direct comparison of the ambient air samples collected on the PUF plugs and the TIGF filters, both the PUF plug and the filter samples were composited identically. Samples collected during day and night collection periods were kept separate, both because of meteorological factors and the differing chemistries of daytime and nighttime ambient atmospheres. The primary criteria used to decide which of the 12-hr collection period samples would be composited for chemical analyses was the need for sufficient particle weight on the filters for a complete chemical analysis of the PAH and PAH-derivatives. Approximately 0.7 g of POM was estimated as the required particle weight, although the use of somewhat lesser

amounts was considered in certain cases to allow analysis of potentially interesting samples, as discussed below.

Additional data utilized to aid in the selection of the samples to composite were:

(a) Mutagenicity data. Specifically, we used the direct activity towards Salmonella typhimurium strain TA98 in terms of revertants per μg of extract (the specific activity), the ratio of the mutagenicities toward strains TA98NR and TA98 and, for the samples collected at Mammoth Lakes, the ratio of the mutagenicities toward strain TA98 with and without added S9.

(b) The percentage of the particulate matter which was extractable into the solvents used (an indication of the relative amounts of organic matter present in the particulate samples).

(c) Meteorological and/or other factors such as the wind direction and, for the Concord and Mammoth Lakes sites, the presence or not of wood smoke odors.

Since the mutagenicity data were an important factor in the recommendations for compositing of the PUF plug and TIGF filter samples, no decisions concerning the compositing of collected samples were made until the mutagen testing had been carried out and the data reduced for a given site. In all cases, our recommendations concerning the samples to be composited were forwarded to the ARB staff for their input and suggestions. Apart from the Glendora samples, for which the ARB had specific recommendations based upon mutagenicity data from the General Motors Research Laboratories (in addition to our own mutagenicity data), all of our recommendations were agreed upon by the ARB staff. In the sections below, the ambient air PUF plug and TIGF filter samples composited, and the rationale behind these choices, are discussed.

Glendora

The ambient air samples collected on TIGF filters at Glendora are given in Table V-1, together with the particulate weights from the remaining five Hi-vols equipped with inlets and available for chemical analysis (two of the original seven Hi-vols equipped with inlets being used for mutagenicity). The maximum ozone data, as monitored by our Dasibi ozone analyzer, and the observation (or lack of observation) of NO_3 radicals

Table V-1. Ambient Air Samples Collected at Glendora, CA, During August 1986

Collection Sample No.	Date	Time (PDT)	Particulate[a] Loading (g)
1	8/12/86	0800-2000[b]	0.42
2	8/12-13/86	2000-0800	0.30
3	8/13/86	0800-2000	0.49
4	8/13-14/86	2000-0800	0.34
5	8/14/86	0800-2000[b]	0.50
6	8/14-15/86	2000-0800	0.21[c]
7	8/15/86	0800-2000	0.39[c]
8	8/15-16/86	2000-0800	0.26
9	8/16/86	0800-2000	0.38
10	8/16-17/86	2000-0800	0.25
11	8/17/86	0800-2000	0.33
12	8/17-18/86	2000-0800	0.23
13	8/18/86	0800-2000	0.52
14	8/18-19/86	2000-0800	0.23
15	8/19/86	0800-2000	0.40
16	8/19-20/86	2000-0800	0.24
17	8/20/86	0800-2000	0.46
18	8/20-21/86	2000-0800	0.28

[a]Particulate loading for five filters from Hi-vols fitted with inlets.
[b]Due to periodic power failures, total sampling time is unknown.
[c]Particulate weight for four filters.

by our differential optical absorption spectroscopic (DOAS) system during early evening hours at this site are given in Table V-2. The maximum ozone levels did not exhibit a marked variation over the period of this study, ranging from ~185-300 ppb. Nitrate radicals, and hence N_2O_5, were present during the evening of August 13; were possibly present at low concentrations on the evenings of August 12, 14, 19 and 20 and were below the detection limit of the DOAS system on the other evenings (see Final Report to ARB Contract No. A5-150-32).

Table V-2. Maximum O_3 Levels and Observations of NO_3 Radicals at Citrus College, Glendora, CA, During August 12-20, 1986

Date	Maximum O_3 Concentration (ppm)	NO_3 Radicals Present
8/12	0.25	No/Possibly[a]
8/13	0.185	Yes
8/14	0.27	Possibly
8/15	0.26	No
8/16	0.24	No
8/17	0.27	No
8/18	0.28	No
8/19	0.30	Possibly
8/20	0.27	Possibly

[a]Long pathlength differential optical absorption system not fully operational.

In previous studies we obtained evidence for the atmospheric formation of 2-nitrofluoranthene from fluoranthene via gas-phase nighttime N_2O_5 reaction (Atkinson et al. 1987a, Zielinska et al. 1988a), and hence proposed to further investigate this possible nitroarene formation pathway. A further criterion for deciding which samples to analyze concerned the mutagenicity data obtained by the General Motors Research Laboratories research group, with the highest mutagenicities being observed as follows: (1) 2000 hr August 20 to 0800 hr August 21, (2) 0800-2000 hr August 20, (3) 0800-2000 hr August 15, (4) 2000 hr August 16 to 0800 hr August 17 and (5) 0800-2000 hr August 12.

Based upon these data, the research objectives of this program and the wishes of the ARB for chemical analyses for several of the time periods noted above, we proposed to composite the PUF plug and filter samples as six PUF plug samples and six TIGF filter samples, as follows: (Note that the collection sample numbers refer to Table V-1.)

Sample #1.	The daytime collection sample #3 (8/13). Day sample to be compared with Sample #2.
Sample #2.	The nighttime collection sample #4 (8/13-14). Night sample when NO_3 radicals were present.
Composite Samples #3 and #3A.	The daytime collection samples #7 (8/15), #9 (8/16), #11 (8/17), #13 (8/18).
Composite Samples #4 and #4A.	The nighttime collection samples #8 (8/15-16), #10 (8/16-17), #12 (8/17-18), #14 (8/18-19).
Sample #5.	The daytime collection sample #17 (8/20). This time period is that of the second highest mutagenicity as measured by General Motors.
Sample #6.	The nighttime collection sample #18 (8/20-21). This time period is that of the highest mutagenicity as measured by General Motors.

Samples #3A and #4A were in essence replicates of Samples #3 and #4, respectively, made up of the filters from the modified Hi-vols with PUFs and one additional filter. These replicates were necessary due to problems in the analytical procedures as detailed in Section VI.

For the composite Samples #1, #2, #3A, #4A, #5 and #6, the azaarene extractions and quantifications were not carried out. The azaarenes were expected to be at very low levels, and we judged that the amount of sample from a single 12-hr collection (Samples #1, #2, #5 and #6) was insufficient to carry out the azaarene analysis. In addition it was anticipated that the interesting species in terms of correlating with the GM mutagenicity were the PAH and nitroarenes. For Samples #3A and #4A, which were extracted with CH_2Cl_2 (see Section VI), the azaarene extraction was not expected to be quantitative (Dong et al. 1977a,b).

PUF plug and TIGF filters from collection samples #1 (8/12), #2 (8/12-13), #5 (8/14), #6 (8/14-15), #15 (8/19) and #16 (8/19-20) have been stored for possible subsequent analysis.

Yuba City

The ambient air samples collected, their approximate particulate loadings, the mutagenicities toward strains TA98 (-S9) and the ratio of mutagenicities TA98/TA98NR and brief comments concerning the sampling conditions are given in Table V-3. Our recommendations for compositing

the filter and PUF plug samples are given below. We grouped the collected samples into those with relatively similar mutagenicities, in terms of rev μg^{-1} extract, with respect to strain TA98. (Note that the collection sample numbers refer to Table V-3.)

Composite Sample #1. The daytime collection samples #1 (10/16), #4 (10/18), #6 (10/20) and #12 (10/25).

Composite Sample #2. The daytime collection samples #3 (10/17) and #10 (10/23).

Composite Sample #3. The nighttime collection samples #2 (10/16-17), #5 (10/18-19), #7 (10/20-21) and #11 (10/23-24).

All of these samples were collected on days when burning occurred or on the nights immediately following burning. For composite Sample #1 the mutagenic activities (in rev μg^{-1}) were all between 0.5-0.9, while for composite Sample #2 these quantities were significantly higher at 1.5-2.1. Because of the low particle loadings observed during the nighttime hours, we proposed to composite all of the samples collected on the nights after a burn day. Collection samples #8 and #9, collected on a day when no burning was carried out and the night of that day (10/21 and 10/21-22, respectively), have been held for possible future analysis.

Concord

The ambient air samples collected, their particulate loadings, the percent extractable, the specific activity toward strain TA98 (-S9) and the ratio of mutagenicities TA98/TA98NR and brief comments concerning the sampling conditions are given in Table V-4. Our choices for compositing the filter and PUF plug samples were based upon having sufficient particle weight to carry out a complete analysis (~0.7 g), on the mutagenicity to strain TA98 (-S9) in terms of revertants per µg of extract, on the percent extractable and on the wind direction.

The samples fell into two general nonoverlapping classes, those with a high (>60%) percent extractable and those with a high mutagenic potency (>2.0 rev μg^{-1}) and these also tended to be associated with differing wind directions. Our groups were: (Note that the collection sample numbers refer to Table V-4.)

Table V-3. Ambient Air Samples Collected at Yuba City, CA, During October 1986

Collection Sample No.	Date	Time (PDT)	Particulate Loading (g)[a]	Mutagenicity TA98(-S9) (rev m^{-3})	Mutagenicity TA98(-S9) (rev μg^{-1} extract)	TA98NR(-S9)/ TA98(-S9)	Comments
1	10/16/86	0700-1900	0.36	24	0.89	0.40	High burn day, 1,900 acres in Yuba Co.
2	10/16-17/86	1900-0700	0.12	4.3	0.51	0.63	Night after high burn day.
3	10/17/86	0700-1700	0.16	24	1.5	0.51	High burn day, 3,300 acres, sampling stopped due to rainstorm.
4	10/18/86	0700-1900	0.11	7.8	0.76	0.54	Low burn day, 448 acres.
5	10/18-19/86	1900-0700	0.06	6.2	0.9	0.42	Night after low burn day.
6	10/20/86	0900-1900	0.22	11	0.46	0.37	Low burn day, 600 acres.
7	10/20-21/86	1900-0700	0.26	36	1.2	0.63	Night after low burn day.
8	10/21/86	0700-1900	0.28	46	2.6	0.50	No burning, light and variable winds.
9	10/21-22/86	1900-0700	0.26	60	2.6	0.54	Night after no burn day.
10	10/23/86	0830-1620	0.20	95	2.1	0.52	Medium burn day; shutdown due to rain.
11	10/23-24/86	2330-0730	0.13	57	2.9	0.52	Night after medium burn day and rainstorm.
12	10/25/86	1000-1700	0.10	7.4	0.58	0.29	High burn day, but very low nephelometer readings and low filter loadings.

[a]Approximate particulate loading for five filters from Hi-vols fitted with inlets.

Table V-4. Ambient Air Samples Collected at Concord, CA, During December 1986 and January 1987

Collection Sample No.	Date	Time (PST)	Particulate[a] Loading (g)	Percent Extractable	Mutagenicity TA98(-S9) (rev μg^{-1} extract)	TA98NR(-S9)/ TA98(-S9)	Comments
1	12/6-7/86	2030-0500	0.19	82	1.0	0.55	Clear, smell of wood smoke, winds SW to W
2	12/7/86	0500-1700	0.05	53	1.4	0.40	Light winds from S
3	12/7-8/86	1700-0500	0.28	87	0.71	0.61	Winds S-E; smell of smoke and diesel
4	12/8/86	0500-1700	0.18	58	2.9	0.48	Winds N-NE
5	12/8-9/86	1700-0500	0.38	75	1.1	0.53	Winds S; smell of wood smoke
6	12/9/86	0500-1700	0.22	60	2.0	0.60	Winds N-NE
7	12/10-11/86	1700-0500	0.27	48	3.0	0.47	Foggy, rain
8	12/12/86	0500-1700	0.22	57	0.86	0.42	Winds E-NNE
9	1/13/87	0900-1700	0.04	47	2.0	0.41	Foggy, windy, from SE. SO_2 observed
10	1/13-14/87	1815-0500	0.14	60	0.58	0.84	Winds N-NW
11	1/14/87	0500-1700	0.11	46	5.0	0.58	Winds S changing to W. SO_2 observed
12	1/14-15/87	1700-0500	0.12	52	3.2	0.47	Windy
13	1/17-18/87	1700-0500	0.50	79	0.71	0.68	Light winds, S

(continued)

Table V-4 (continued) - 2

Collection Sample No.	Date	Time (PST)	Particulate[a] Loading (g)	Percent Extractable	Mutagenicity TA98(-S9) (rev μg^{-1} extract)	TA98NR(-S9)/ TA98(-S9)	Comments
14	1/18/87	0500-1700	0.38	81	1.2	0.43	No wind until 1200 hr, then N
15	1/18-19/87	1700-0500	0.45	70	0.78	0.49	
16	1/19/87	0500-1422	0.22	55	3.7	0.43	Strong winds, N. Early shutdown due to winds
17	1/21/87	0500-1700	0.34	74	1.2	0.49	Light winds from S, N wind at refinery
18	1/21-22/87	1700-0500	0.53	67	1.2	0.70	Light winds from S
19	1/22/87	0500-1600	0.43	72	1.7	0.44	Winds N-E, rained at 1600 hr

[a]Particulate loading for five filters from Hi-vols fitted with inlets.

Composite Sample #1. The daytime collection samples #4 (12/8), #6 (12/9) and #16 (1/19) obtained with generally northerly winds. We considered adding samples #9 (1/13) and #11 (1/14) as well, but since these had winds generally from the south, we recommended not doing so. Additionally, sample #9 had a very low mass of 0.04 g.

Composite Sample #2. The daytime collection samples #14 (1/18), #17 (1/21) and #19 (1/22). These had high percents extractable and low mutagenic potencies.

Composite Sample #3. The nighttime collection samples #1 (12/6-7), #3 (12/7-8) and #5 (12/8-9) were obtained under conditions when wood smoke was present. All had a high percent extractable and winds were generally from the south.

Composite Sample #4. The nighttime collection samples #13 (1/17-18), #15 (1/18-19) and #18 (1/21-22). These were similar to those in composite Sample #3 above, but wood smoke was not evident during these sampling conditions.

Composite Sample #5. The nighttime collection samples #7 (12/10-11) and #12 (1/14-15), which had high mutagenic potency.

This left us with collection samples #2 (12/7), #8 (12/12), #9 (1/13), #10 (1/13-14) and #11 (1/14), of which samples #2 and #10 had very low particle weights. We recommended that collection sample #11, with the highest mutagenic potency observed at this location, be held for possible future analysis, and that samples #2, #8, #9 and #10 not be analyzed.

Mammoth Lakes

The ambient air samples collected, the particulate loadings, the percent extractable and the specific activity toward strain TA98 and the ratio of mutagenicities of TA98/TA98NR and TA98(+S9)/TA98(-S9) are given in Table V-5. Our choices for compositing the filter and PUF plug samples were based upon having sufficient particle weight to carry out a complete chemical analysis (~0.7 g), on the percent extractable, the ratio of the responses to strain TA98 with and without S9, the ratio of the response to TA98NR relative to TA98 (-S9) and the mutagenicity to strain TA98 (-S9) in terms of revertants per μg of extract.

Our groupings were: (Note that the collection sample numbers refer to Table V-5.)

Table V-5. Ambient Air Samples Collected at Mammoth Lakes, CA, During February and March 1987

Collection Sample No.	Date	Time (PST)	Particulate Loading (g)[a]	Percent Extractable	Mutagenicity TA98(-S9) (rev μg^{-1} extract)	TA98(+S9)/ TA98(-S9)	TA98NR(-S9)/ TA98(-S9)
1	2/14/87	0500-1700	0.12	76	0.34	2.1	0.38
2	2/14/87	1700-2330	0.08	55	0.20	2.8	0.42
3	2/15-16/87	1730-0500	0.21	88	0.13	1.8	0.49
4	2/16/87	0500-1700	0.09	50	0.14	5.1	0.64
5	2/16-17/87	1700-0500	0.37	87	0.094	4.6	0.72
6	2/17/87	0500-1700	0.04	51	0.20	2.9	0.55
7	2/17-18/87	1700-0500	0.25	92	0.13	2.1	0.69
8	2/20-21/87	1700-0500	0.33	89	0.17	5.5	0.82
9	2/21/87	0500-1700	0.12	42	0.54	1.4	0.31
10	2/21-22/87	1700-0500	0.12	41	0.11	5.8	1.0
11	2/22/87	0500-1700	0.12	41	1.1	1.4	0.53
12	2/22-23/87	1700-0500	0.09	28	0.62	1.2	0.40
13	2/25-26/87	1700-0500	0.08	80	0.089	1.9	0.52
14	2/26/87	0500-1700	0.06	75	0.21	3.9	0.52
15	2/27-28/87	1700-0500	0.44	97	0.061	5.1	0.85
16	2/28/87	0500-1700	0.13	8	0.42	3.1	0.57
17	2/28-3/1/87	1700-0500	0.43	86	0.11	4.2	0.69

[a]Particulate loading for five filters from Hi-vols fitted with inlets.

Composite Sample #1. The daytime collection samples #1 (2/14), #4 (2/16), #6 (2/17), #9 (2/21), #11 (2/22), #14 (2/26) and #16 (2/28). The total particulate weight for these seven daytime samples, for the five filter samples collected by Hi-vol samplers equipped with inlets, was 0.69 g, just sufficient for a complete analysis.

Composite Sample #2. The nighttime collection samples #5 (2/16-17), #7 (2/17-18), #8 (2/20-21), #15 (2/27-28) and #17 (2/28-3/1) which had >60% extractable weight, a high ratio (>0.6) of response to TA98NR relative to response to TA98 (-S9), a high ratio of response to TA98 in the presence of S9 compared to the absence of S9 (>2) and a relatively high mutagenic potency to TA98. This composite sample had a total particulate weight of 1.82 g.

Composite Sample #3. The remaining nighttime collection samples #2 (2/14), #3 (2/15-16), #10 (2/21-22), #12 (2/22-23) and #13 (2/25-26). This composite sample had a total particulate mass of 0.58 g, again just sufficient for a complete chemical analysis.

Oildale

The ambient air samples collected, the particulate loadings, the percent extractable and the specific activity towards strain TA98 and the ratio of mutagenicities TA98/TA98NR are given in Table V-6. Our recommendations for compositing the filter and PUF plug samples were based upon having sufficient particle weight to carry out a complete chemical analysis (~0.7 g), on the percent extractable, the ratio of the responses to strain TA98 with and without S9 and the mutagenicity to strain TA98 (-S9) in terms of revertants per μg of extract.

Our groupings were: (Note that the collection sample numbers refer to Table V-6.)

Composite Sample #1. All of the daytime collection samples [#2 (3/30), #3 (3/31), #5 (4/1), #7 (4/2), #8 (4/7), #10 (4/8), #12 (4/9) and #14 (4/10)]. The majority of these daytime samples had similar characteristics, with only samples #2 and #3 having mutagenicities of >1 rev μg^{-1} extract. Since these two samples did not have sufficient particle loading for a separate chemical analysis, we recommended including them in a single composited daytime sample. This composite sample had a particulate mass of 1.349 g.

Table V-6. Ambient Air Samples Collected at Oildale, CA, During March and April of 1987

Collection Sample No.	Date	Time (hr)[a]	Particulate Loading (g)[b]	Percent Extractable	Mutagenicity TA98(-S9) (rev μg^{-1}) extract	TA98NR(-S9)/ TA98(-S9)
1	3/29-30/87	1800-0600	0.09	18	0.93	0.56
2	3/30/87	0600-1800	0.13	15	1.1	0.54
3	3/31/87	0745-1800	0.15	15	1.2	0.38
4	3/31-4/1/87	1800-0600	0.19	26	1.1	0.55
5	4/1/87	0600-1800	0.19	22	0.65	0.37
6	4/1-2/87	1800-0600	0.18	14	1.3	0.31
7	4/2/87	0600-1800	0.17	28	0.65	0.31
8	4/7/87	0700-1900	0.16	32	0.53	0.43
9	4/7-8/87	1900-0700	0.29	15	1.8	0.42
10	4/8/87	0700-1900	0.17	24	0.65	0.29
11	4/8-9/87	1900-0700	0.24	22	1.3	0.43
12	4/9/87	0700-1900	0.17	21	0.78	0.31
13	4/9-10/87	1900-0700	0.23	30	0.72	0.58
14	4/10/87	0700-1900	0.20	22	0.59	0.31
15	4/10-11/87	1900-0700	0.18	23	0.39	0.51

[a]Times are PST for 3/29 through 4/2; PDT for 4/7 through 4/11.
[b]Particulate loading for five filters from Hi-vols fitted with inlets.

Composite Sample #2. The nighttime collection samples [#1 (3/29-30), #13 (4/9-10) and #15 (4/10-11)], all of which had low (<1 rev μg^{-1}) mutagenicities towards TA98 (-S9) and response ratios (-S9) of TA98NR/TA98 of >0.50. The particulate weight of these three 12-hr samples was 0.50 g, just sufficient to carry out a full chemical analysis.

Composite Sample #3. The nighttime collection samples [#4 (3/31-4/1), #6 (4/1-2), #9 (4/7-8) and #11 (4/8-9)] all of which had relatively high mutagenicities towards TA98 (-S9) and low ratios of response towards TA98NR relative to that towards TA98. The particulate weight was 0.90 g.

Reseda

The samples collected, the particulate loadings, the percent extractable and the specific activity towards strain TA98 and the ratio of mutagenicities TA98NR/TA98 are given in Table V-7. Our recommendations for compositing the filter and PUF plug samples were based upon having sufficient particle weight to carry out a complete chemical analysis (~0.7 g), on the percent extractable, the ratio of the responses to strain TA98 with and without S9, the mutagenicity to strain TA98 (-S9) in terms of revertants per µg of extract and the ambient naphthalene concentrations (available from the individual 12-hr Tenax-GC solid adsorbent samples).

Our groupings were: (Note that the collection sample numbers refer to Table V-7.)

Composite Sample #1. All of the daytime collection samples [#2 (5/28), #4 (5/29), #6 (5/30), #8 (5/31), #10 (6/1), #12 (6/2), #15 (6/14) and #17 (6/15)]. The majority of these daytime samples had similar characteristics. The particulate weight was 1.45 g.

Composite Sample #2. The nighttime collection samples #1 (5/27-28), #3 (5/28-29), #5 (5/29-30), #7 (5/30-31), #9 (5/31-6/1), #11 (6/1-2), #13 (6/2-3), #14 (6/13-14) and #16 (6/14-15), all of which again had similar characteristics. The particulate weight was 1.73 g.

In particular, apart from a generally distinct day/night variation, the ambient naphthalene concentrations exhibited no major fluctuations during this sampling period, although the last three samples (#15-17) indicated a generally cleaner air mass sampled.

Table V-7. Ambient Air Samples Collected at Reseda, CA, May and June 1987

Collection Sample No.	Date	Time Period (PDT)	Particulate Weight (g)[a]	Percent Extractable	Mutagenicity TA98(-S9) (rev μg^{-1} extract)	TA98NR(-S9)/ TA98(-S9)	Naphthalene Concentration (ng m^{-3})
1	5/27-28/87	2000-0700	0.14	46	1.5	0.57	995
2	5/28/87	0700-1900	0.16	28	2.1	0.35	520
3	5/28-29/87	1900-0700	0.14	42	1.4	0.56	1300
4	5/29/87	0700-1900	0.21	38	1.1	0.35	750
5	5/29-30/87	1900-0700	0.17	48	1.4	0.46	1400
6	5/30/87	0700-1900	0.19	35	0.94	0.35	370
7	5/30-31/87	1900-0700	0.22	43	1.5	0.47	-[b]
8	5/31/87	0700-1900	0.19	36	0.99	0.31	410
9	5/31-6/1/87	1900-0700	0.21	42	2.3	0.39	1600
10	6/1/87	0700-1900	0.18	38	1.4	0.35	340
11	6/1-2/87	1900-0700	0.22	26	1.1	0.34	1600
12	6/2/87	0700-1900	0.23	38	1.4	0.33	650
13	6/2-3/87	1900-0700	0.26	61	0.66	0.48	985
14	6/13-14/87	1900-0700	0.29	42	0.85	0.42	710
15	6/14/87	0700-1900	0.17	30	0.73	0.36	350
16	6/14-15/87	1900-0700	0.08	41	0.89	0.51	350
17	6/15/87	0700-1900	0.12	26	0.67	0.27	450

[a]Particulate loading for five filters from Hi-vols fitted with inlets.
[b]Not quantified due to missing internal standard.

Pt. Arguello

The ambient air samples collected at Pt. Arguello are given in Table V-8. For these samples, the low mutagenicities (<1 rev m^{-3}) and the concurrent low ambient concentrations of naphthalene (40-200 ng m^{-3}, an order of magnitude lower than those observed at Reseda) mandated that we composite the twenty 12-hr filter samples (collected using only four, instead of our previous five, Hi-vol samplers with inlets) into one single daytime sample and one single nighttime sample for chemical analysis.

San Nicolas Island

The 12-hr filter samples collected at San Nicolas Island during the summertime SCAQS are given in Table V-9. A single Hi-vol sampler fitted with an inlet was used, with the collection periods being started at 0100 and 1300 hr. In view of this and the small amount of material present, we recommended compositing the entire set of samples into one sample for chemical analysis.

As noted above, the ARB staff agreed with these recommendations for the compositing of the PUF plug and TIGF filter samples from these sites, and accordingly these samples were composited as per the above discussion. A listing of the composited PUF plug and TIGF filter samples analyzed is given in Table V-10, and a listing of the total number of samples analyzed is given in Table V-11.

Table V-8. Ambient Air Samples Collected at Pt. Arguello, Vandenberg AFB, CA, During July 1987

Collection Sample No.	Date	Time (PDT)
1	7/4/87	0700-1900
2	7/4-5/87	1900-0700
3	7/5/87	0700-1900
4	7/5-6/87	1900-0700
5	7/6/87	0700-1900
6	7/6-7/87	1900-0700
7	7/7/87	0700-1900
8	7/7-8/87	2045-0700
9	7/8/87	0700-1900
10	7/8-9/87	1900-0700
11	7/9/87	0700-1900
12	7/9-10/87	1900-0700
13	7/10/87	0700-1900
14	7/10-11/87	1900-0700
15	7/11/87	0700-1900
16	7/11-12/87	1900-0700
17	7/12/87	0700-1900
18	7/12-13/87	1900-0700
19	7/13/87	0700-1900
20	7/13-14/87	1900-0700

Table V-9. Ambient Air Samples Collected at San Nicolas Island, CA, During Summertime SCAQS, 1987[a]

Collection Sample No.	Date	Time (PDT)
1	6/19/87	0100-1300
2	6/19-20/87	1300-0100
3	6/24/87	0100-1305
4	6/24-25/87	1305-0100
5	6/25/87	0100-1300
6	6/25-26/87	1300-0100
7	7/13/87	0100-1709
8	7/13-14/87	1710-0040
9	7/14/87	0040-1245
10	7/14-15/87	1247-0045
11	7/15/87	0100-1245
12	7/15-16/87	1250-0042
13	8/27/87	0100-1250
14	8/27-28/87	1300-0100
15	8/28/87	0100-1245
16	8/28-29/87	1300-0100
17	8/29/87	0100-1245
18	8/29-30/87	1300-0100
19	9/2/87	0100-1250
20	9/3/87	0100-1245
21	9/3-4/87	1300-0040

[a]Samples #13-21 were not refrigerated until reaching Riverside.

Table V-10. Summary Table of Sample Compositing and Volume Sampled for the Seven Sampling Sites in California and San Nicolas Island

Location and Composite Sample No.	Day/ Night	Total Volume PUF Samples (m^3)	Total Volume Filter Samples (m^3)	Sampling Interval	Sampling Dates
Glendora Sample #1	Day	469	4,078	0800-2000 PDT	8/13/86
Glendora Sample #2	Night	938	4,078	2000-0800 PDT	8/13-14/86
Glendora Sample #3	Day	3,751	13,048	0800-2000 PDT	8/15,16,17,18/86
Glendora Sample #3A[a]	Day	-	5,158	0800-2000 PDT	8/15,16,17,18/86
Glendora Sample #4	Night	3,751	13,048	2000-0800 PDT	8/15-16,16-17,17-18,18-19/86
Glendora Sample #4A[a]	Night	-	5,627	2000-0800 PDT	8/15-16,16-17,17-18,18-19/86
Glendora Sample #5	Day	938	4,078	0800-2000 PDT	8/20/86
Glendora Sample #6	Night	938	4,078	2000-0800 PDT	8/20-21/86
Yuba City Sample #1	Day	3,415	14,461	0700-1900 PDT	10/16,18,20/86
Yuba City Sample #2	Day	1,475	6,290	0700-1900 PDT	10/17,23/86
Yuba City Sample #3	Night	3,700	15,501	1900-0700 PDT	10/16-17,18-19,20-21,23-24/86
Concord Sample #1	Day	2,874	12,143	0500-1700 PST	12/8,9/86; 1/19/87
Concord Sample #2	Day	2,956	12,737	0500-1700 PST	1/18,21,22/87
Concord Sample #3	Night	2,717	11,827	1700-0500 PST	12/6-7,7-8,8-9/86
Concord Sample #4	Night	3,040	13,101	1700-0500 PST	1/17-18,18-19,21-22/87
Concord Sample #5	Night	1,951	8,734	1700-0500 PST	12/10-11/86; 1/14-15/87
Mammoth Lakes Sample #1	Day	6,234	22,320	0500-1700 PST	2/14,16,17,21,22,26,28/87
Mammoth Lakes Sample #2	Night	4,506	15,943	1700-0500 PST	12/16-17,17-18,20-21,27-28;2/28-3/1/87
Mammoth Lakes Sample #3	Night	4,480	13,475	1700-0500 PST	2/14-15,15-16,21-22,22-23,25-26/87
Oildale Sample #1	Day	8,070	31,641	0600-1800 PST	3/30,31/87; 4/1,2,7,8,9,10/87
Oildale Sample #2	Night	3,113	12,086	1800-0600 PST	3/29-30/87; 4/9-10,10-11/87
Oildale Sample #3	Night	4,151	16,114	1800-0600 PST	3/31-4/1/87; 4/1-2,7-8,8-9/87

(continued)

Table V-10 (continued) - 2

Location and Composite Sample No.	Day/ Night	Total Volume PUF Samples (m^3)	Total Volume Filter Samples (m^3)	Sampling Interval	Sampling Dates
Reseda Sample #1	Day	8,188	30,728	0700-1900 PDT	5/28,29,30,31/87; 6/1,2,14,15/87
Reseda Sample #2	Night	9,326	34,436	1900-0700 PDT	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	9,138	29,211	0700-1900 PDT	7/4,5,6,7,8,9,10,11,12/87
Pt. Arguello Sample #2	Night	8,150	25,492	1900-0700 PDT	7/4-5,5-6,6-7,7-8,8-9,9-10,10-11,11-12/87
San Nicolas Island	Single composite of all samples	-	17,641	0100-1300 PDT	6/19,24,25/87; 7/13,14,15/87; 8/27,28,29/87 9/2,3/87
				1300-0100 PDT	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

[a]Samples 3A and 4A are repeat composites consisting of two filters from the modified Hi-vols with PUF plugs and one additional filter from each sampling period. These repeat composites were necessary due to analytical difficulties; for a full discussion see Section VI.

Table V-11. Summary of the Number of Samples Analyzed at the Seven Sampling Sites in California and San Nicolas Island

Sampling Site	Chemical Analysis				Mutagenicity Analysis
	Tenax		PUF Plug	TIGF Filter	
	Low Flow	High Flow			
Glendora	18	15	6	8	18
Yuba City	12	2	3	3	12
Concord	19	2	5	5	19
Mammoth Lakes	18	2	3	3	17
Oildale	15	2	3	3	15
Reseda	16	2	2	2	17
Pt. Aguello	20	2	2	2	4
San Nicolas Island	0	0	0	1	0

VI. EXTRACTION, FRACTIONATION AND ANALYSIS PROTOCOLS

As noted above in Section III, three media were used for the collection of PAH and PAH-derivatives from ambient air; namely Tenax-GC solid adsorbent, PUF plugs and TIGF filters. The procedures for the extraction of these media and the subsequent fractionation and analysis of these extracts are described below.

A. Tenax-GC Cartridges

The polymer adsorbent Tenax-GC (a polymer of 2,6-diphenyl-p-phenylene oxide) is suitable for sampling vapor phase components from ambient air. Due to the relatively small volumes which were sampled over 12 hours on the low-flow (~0.6 m^3) and high-flow (~6 m^3) Tenax-GC cartridges in comparison with the volumes sampled with even the modified Hi-vols with PUF plugs (~500 m^3), any particles physically trapped by the glass-wool plugs or the Tenax adsorbent itself would generally not contain sufficient PAH for measurement. Thus, the PAH observed on the Tenax cartridges will be abundant, and generally gas-phase, species.

Potentially, any of the PAH or PAH-derivatives on our target lists for monitoring which are present in the gas-phase could be sampled on the Tenax-GC cartridges. From prior analyses conducted at Torrance, CA (Arey et al. 1987), it was anticipated that naphthalene levels would be sufficiently high to be quantifiable by sampling on the low-flow Tenax and using solvent desorption. We utilized back-up Tenax cartridges on the low-flow Tenax to check for any naphthalene breakthrough and operated the high-flow Tenax in an attempt to quantify species less abundant than naphthalene. The initial Tenax samples were screened for the PAH from M.W. 128 to 178, as well as for the hetero-PAH quinoline, isoquinoline and dibenzothiophene and for the nitronaphthalenes. Only the PAH were sufficiently abundant to quantify, and of the targeted PAH recommended for monitoring (Table II-5) only naphthalene was present in the gas-phase in sufficient amounts to quantify from the low-flow Tenax samples.

Prior to extraction and analysis, deuterated internal standards were added to the low- and high-flow Tenax cartridges, respectively, as follows (in μg): naphthalene-d_8 (4.10, 15.85), biphenyl-d_{10} (0.55, 1.02), and phenanthrene-d_{10} (0.58, 0.58). For the low-flow Tenax cartridges from

Glendora, the amounts of deuterated internal standards were somewhat different being: naphthalene-d_8, 1.84 µg, biphenyl-d_{10}, 0.66 µg, and phenanthrene-d_{10}, 0.56 µg. The low- and high-flow cartridges were eluted with 2 mL and 10 mL, respectively, of diethyl ether, which was then solvent exchanged (using a micro-Snyder apparatus for the high-flow cartridges) to ~0.2 mL of acetonitrile.

The samples were analyzed with a Hewlett-Packard 5890 GC equipped with a 7673A Automatic Sampler and interfaced to a 5970 Mass Selective Detector (MSD). A 30 m DB-5 capillary column (J&W Scientific, Inc.) was used, with injections in the splitless mode. Identifications and quantifications of the PAH were made by multiple ion detection (MID), monitoring the molecular ion of each PAH. Authentic standards of all compounds identified (see D below) were available for retention time matching.

Calibration curves for the GC/MS/MID quantification of the PAH were made for the molecular ion peaks of the PAH using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as an internal standard. The National Bureau of Standards SRM 1647 (certified PAH) with the addition of biphenyl, methylnaphthalenes, dibenzothiophene and the deuterated internal standards was utilized to make the calibration solutions.

Results of the quantifications for naphthalene from 12-hr low-flow Tenax samples from each of the seven sites are given in Section VII. Data on volatile PAH (generally not species included on the lists to be monitored) from the complete set of 12-hr high-flow Tenax samples from Glendora and a single 12-hr day and 12-hr night high-flow Tenax sample from each of the other six sites are also given in Section VII.

B. PUF Plugs

Prior to analysis, the PUF plugs from each sampling site were combined to make several day and several night samples with a minimum of a single day sample composite and a single night sample composite for each of the seven sites. As described in detail in Section V, this resulted in twenty-four PUF plug composite samples (Table V-10). Three PUF plugs were employed in each of two modified Hi-vol samplers at each sampling site, with the exception of the Glendora sampling site, where four PUF plugs

were used in the modified Hi-vol samplers. All three, or four, PUF plugs from a single Hi-vol were combined for extraction, with the exception of Glendora Samples #3 and #4 for which the fourth PUF plugs were combined and extracted separately to check for breakthrough of the more volatile of the PAH collected. Prior to extraction, the combined PUF plugs were spiked with deuterated internal standards at the concentrations given in Table VI-1. All samples were Soxhlet extracted overnight (~16 hr) with CH_2Cl_2, and then concentrated by rotary evaporation under vacuum to ~2 mL and filtered through 0.45 μm Acrodiscs (Gelman Sci.), rinsing the sample flask twice with 1 mL CH_2Cl_2 each time and concentrating further under a stream of nitrogen to a final volume of ~500 μL.

The extracts were fractionated by high performance liquid chromatography (HPLC) using an Altex semi-preparative scale Ultrasphere Silica column (1 cm x 25 cm). The HPLC system consisted of a Spectra-Physics Model 8100 chromatograph, Model 4100 computing integrator, Model 8400 uv/visible detector and an ISCO fraction collector. Figure VI-1 shows a typical HPLC profile of a PUF plug extract together with the mobile phase program employed (using a flow rate of 3 mL min^{-1}). A fraction containing the PAH was collected from 4 min to 22 min (subfractions 3-7, Figure VI-1) and a nitroarene-containing fraction from 22 min to 34 min (subfractions 8-11). The more polar subfractions were collected and stored for future analysis. The fractions were concentrated by rotary evaporation, then taken just to dryness under a stream of nitrogen. The PAH fractions were dissolved in acetonitrile and the nitroarene fractions in CH_2Cl_2 prior to analysis by GC/MS/MID using the Hewlett-Packard 5970 MSD. Injections were made in the splitless mode onto either a 30 m DB-5 (J&W Scientific, Inc.) or a 50 m 5% PhMe Silicone (Hewlett-Packard) capillary column.

The molecular ions of the following PAH, PASH and deuterated PAH were monitored in the PAH fractions: fluorene, phenanthrene, phenanthrene-d_{10}, anthracene, anthracene-d_{10}, dibenzothiophene, dibenzothiophene-d_8, fluoranthene, fluoranthene-d_{10}, pyrene, pyrene-d_{10}, benz[a]anthracene, benz[a]anthracene-d_{12}, chrysene/triphenylene and chrysene-d_{12}. Identifications were based on retention time matching of the molecular ion peaks and quantifications were made on the basis of the deuterated internal standards as discussed above for the Tenax samples. Results of the quantifications of these PAH and PASH, with the exception of benz[a]anthracene and chrysene/

Table VI-1. The Amounts (μg) of Deuterated Standards Added to the Combined PUF Samples Prior to Extraction

	Site and Composite Sample Number[a]														
	Glendora				Yuba City		Concord			Mammoth Lakes		Oildale		Reseda	Pt. Arguello
Deuterated Standards	#1	#2,#5,#6	#3,#4	4th PUF	#1,#3	#2	#1,#3	#2,#4	#5	#1,#3	#2	#1,#3	#2	#1,#2	#1,#2
Naphthalene-d_8	2.48	3.27	9.92	2.48	7.44	3.97	4.96	9.92	3.97	4.96	9.92	10.80	5.40	10.80	5.40
Biphenyl-d_{10}	2.48	3.27	9.91	2.48	7.43	3.96	4.96	9.91	3.96	4.96	9.91	9.84	4.92	9.84	4.92
Phenanthrene-d_{10}	2.50	3.30	10.01	2.50	15.00	8.00	10.00	20.00	8.00	10.01	20.02	20.96	10.48	20.96	10.48
Anthracene-d_{10}	2.79	3.69	11.19	2.79	8.39	4.48	5.60	11.19	4.48	5.60	11.19	12.41	6.20	12.41	6.20
Fluoranthene-d_{10}	2.66	3.51	10.64	2.66	7.98	4.26	5.32	10.64	4.26	5.32	10.64	10.64	5.32	10.64	5.32
Pyrene-d_{10}	2.62	3.45	10.46	2.62	7.85	4.18	5.23	10.46	4.18	5.23	10.46	10.46	5.23	10.46	5.23
Benz[a]anthracene-d_{12}	1.02	1.34	4.06	1.02	3.05	1.62	2.03	4.06	1.62	3.03	6.02	4.26	2.13	4.26	2.13
Chrysene-d_{12}	2.11	2.78	8.43	2.11	6.32	3.37	4.22	8.43	3.37	4.22	8.43	8.12	4.06	8.12	4.06
Dibenzothiophene-d_8	0.77	1.02	3.08	0.77	2.31	1.23	1.54	3.08	1.23	1.54	3.08	3.08	1.54	3.08	1.54
Carbazole-d_8	0.76	1.01	3.05	0.76	2.29	1.22	1.52	3.05	1.22	1.52	3.05	3.05	1.52	3.05	1.52
1-Nitronaphthalene-d_7	0.27	0.35	1.07	0.27	1.61	0.86	1.07	2.14	0.86	1.07	2.14	2.15	1.08	2.15	1.08
2-Nitrofluoranthene-d_9	0.27	0.35	1.07	0.27	1.61	0.86	1.07	2.14	0.86	1.07	2.14	2.14	1.07	2.14	1.07
1-Nitropyrene-d_9	b	b	b	b	1.51	0.80	1.00	2.01	0.80	1.00	2.01	2.01	1.00	2.01	1.00
9-Nitroanthracene-d_9	c	c	c	c	c	c	1.11	2.22	1.11	1.11	2.22	2.22	1.11	2.22	1.11
Acridine-d_9	1.28	1.68	5.10	1.28	3.83	2.04	2.55	5.10	2.04	2.55	5.10	5.10	2.55	5.10	2.55
Quinoline-d_7	1.36	1.80	5.46	1.36	4.10	2.18	2.73	5.46	2.18	2.73	5.46	5.25	2.62	5.25	2.62

[a]See Table V-10 for a complete listing of the composited samples.
[b]Not added.
[c]Not available at the time of analysis.

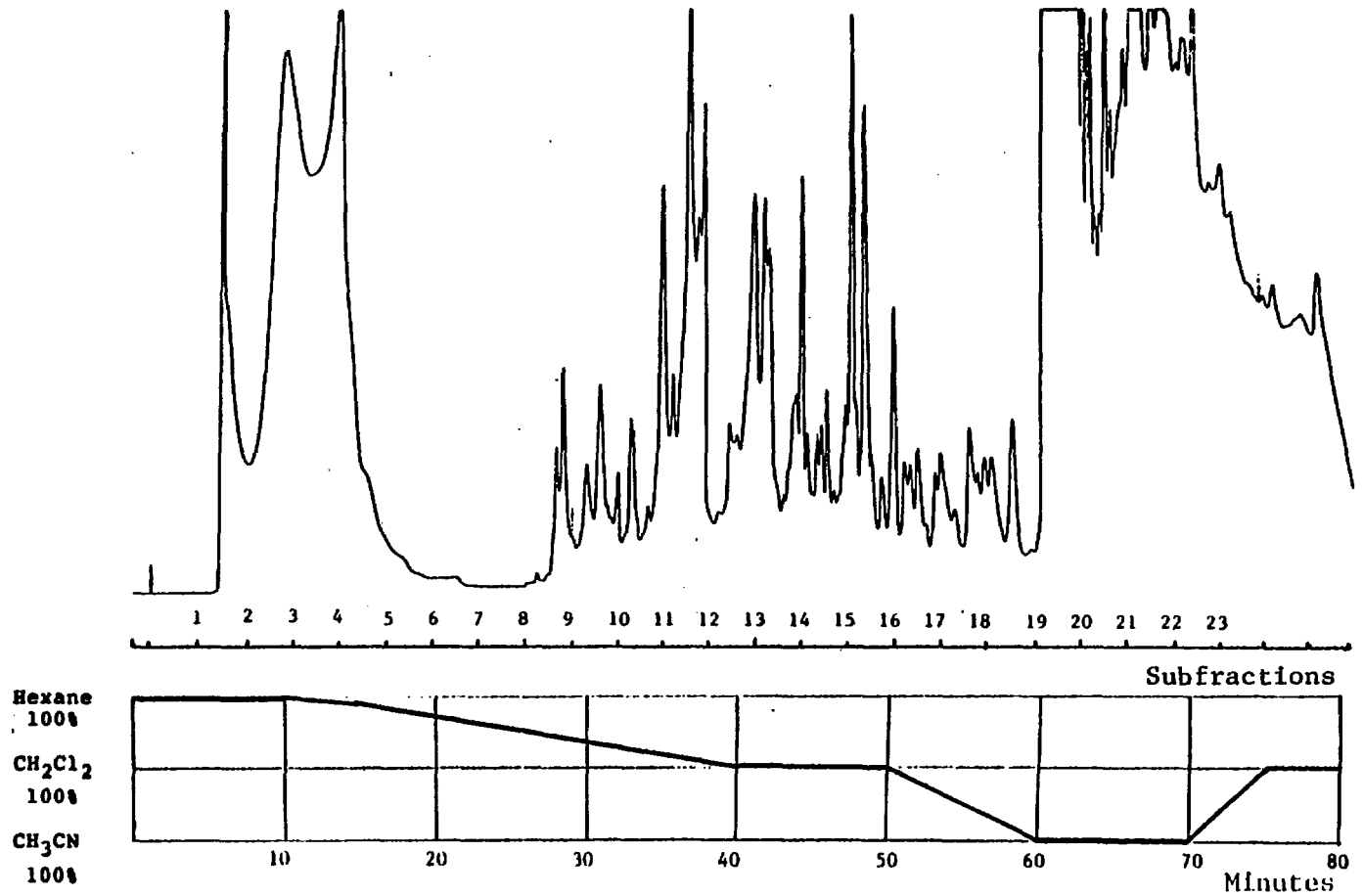


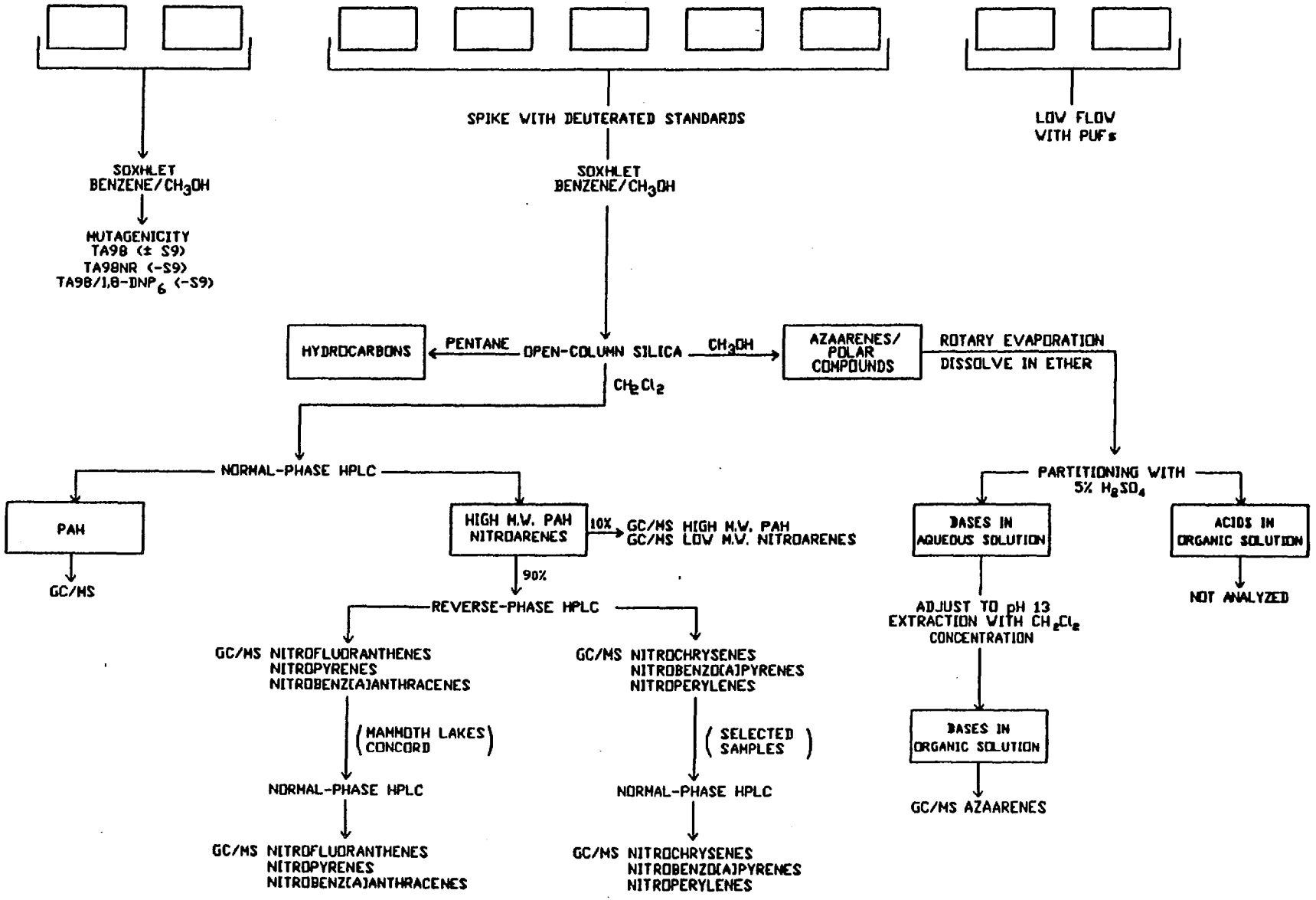
Figure VI-1. HPLC trace (254 nm) and gradient solvent program for separation of an ambient sample collected on PUF plugs. HPLC subfractions were combined as follows: 3-7, 8-11, 12, 13-15, 16-23.

triphenylene which were not sufficiently abundant to quantify (they were quantified from the filter extracts), are given in Section VII.

Unlike the PAH for which the molecular ion, $[M]^+$, is the most abundant ion in their spectra, the nitroarenes have abundant fragment ions generally including the following: $[M-NO]^+$, $[M-NO_2]^+$, $[M-HNO_2]^+$, $[M-NO-CO]^+$ (see Appendix B for spectra of several nitroarenes). The molecular ions and characteristic fragment ions of the nitroarenes were monitored as follows: nitronaphthalenes (m/z: 173, 145, 143, 127, 126, 115), 1-nitronaphthalene-d_7 (m/z: 180, 152, 134, 122), methylnitronaphthalenes (m/z: 187, 170 or 140, 159 or 157, 141, 115), nitrobiphenyls and nitroacenaphthenes (m/z: 199, 153, 152, 151, 141), nitrofluorene (m/z: 211, 165, 164), nitroanthracenes and nitrophenanthrenes (m/z: 223, 193, 177, 176, 165), and (where included, see Table VI-1) 9-nitroanthracene-d_9 (m/z: 232, 186, 184). 1- and 2-Nitronaphthalene and 3-nitrobiphenyl were quantified on the basis of their molecular ion peaks using calibration curves with 1-nitronaphthalene-d_7 as the internal standard (see Section VII).

C. TIGF Filters

Extraction and HPLC Separations. As described in Section V, the TIGF filters from the seven sampling sites were composited into several day and night samples. The filters from the eighth sampling site, San Nicolas Island, were combined into a single sample. The filter extraction and work-up procedure was as shown in Scheme VI-1. Prior to extraction, each sample was spiked with deuterated internal standards at the concentrations listed in Table VI-2. The filters were Soxhlet extracted overnight (16 hr) with benzene/methanol (4/1 v/v), a solvent system chosen to ensure efficient extraction of the azaarenes (Dong et al. 1977a,b) while avoiding the potential for mutagenicity artifacts (Goto et al. 1981) associated with acetonitrile, the polar solvent we have used previously. The replicate, Glendora Samples #3A and #4A were extracted with CH_2Cl_2 (see below). The extracts were concentrated by rotary evaporation and pre-cleaned by open-column silica chromatography. Silicic acid (Mallinckrodt, 100 mesh) was pre-washed with methanol (CH_3OH) and reactivated by heating in an oven to 400°C [a previous deactivation step (Winer et al. 1987) was eliminated to improve azaarene recovery as discussed below]. Sequential



Scheme VI-1. Outline of the chemical analysis procedure for PAH, nitroarenes and azaarenes in ambient POM samples.

Table VI-2. The Amounts (μg) of Deuterated Standards Added to the Combined TIGF Filter Samples Prior to Extraction

Deuterated Standards	Site and Composite Sample Number[a]																
	Glendora			Yuba City		Concord				Mammoth Lakes		Oildale			Reseda	Pt. Arguello	San Nicolas Island
	#1,#2 #5,#6	#3,#4	#3A,#4A	#1	#2,#3	#1,#5	#2	#3	#4	#1,#3	#2	#1	#2	#3	#1,#2	#1,#2	
Fluoranthene-d_{10}	10.60	31.90	15.90	5.10	2.55	2.55	5.10	3.82	5.10	2.55	6.38	5.10	2.55	3.82	5.10	2.55	1.91
Pyrene-d_{10}	10.40	31.40	15.60	5.02	2.51	2.51	5.02	3.76	5.02	2.51	6.28	5.02	2.51	3.76	5.02	2.51	1.88
Benz[a]anthracene-d_{12}	2.13	6.38	3.20	4.26	2.13	2.13	4.26	3.20	4.26	2.13	5.32	4.26	2.13	3.20	4.26	2.13	1.60
Chrysene-d_{12}	5.27	15.8	7.90	10.54	5.27	5.27	10.54	7.90	10.54	4.06	10.15	8.12	4.06	6.09	8.12	4.06	3.04
Benzo[a]pyrene-d_{12}	2.82	8.44	4.22	5.62	2.81	2.82	5.63	4.23	5.63	2.82	7.05	5.64	2.82	4.23	5.64	2.82	2.12
Perylene-d_{12}	1.05	3.14	1.58	2.10	1.05	1.36	2.41	1.88	2.41	1.36	3.40	2.72	1.36	2.04	2.72	1.36	1.02
Dibenz[a,h]anthracene-d_{14}	1.98	5.93	2.97	11.86	5.93	5.93	11.86	8.90	11.86	5.93	14.82	11.86	5.93	8.90	11.86	5.93	4.45
Carbazole-d_8	2.03	6.10	3.04	4.06	2.03	2.03	4.06	3.04	4.06	2.03	5.08	4.06	2.03	3.04	4.06	2.03	1.52
Dibenzothiophene-d_8	2.06	6.16	3.09	4.12	2.06	2.06	4.12	3.09	4.12	2.06	5.15	4.12	2.06	3.09	4.12	2.06	1.54
Quinoline-d_7	3.28	9.84	4.92	6.56	3.28	3.28	6.86	4.92	6.86	3.28	8.20	6.56	3.28	4.92	6.56	3.28	2.46
Acridine-d_9	3.06	9.18	4.59	6.12	3.06	3.06	6.12	4.59	6.12	3.06	7.65	6.12	3.06	4.59	6.12	3.06	2.30
1-Nitronaphthalene-d_7	0.54	1.61	0.81	1.08	0.54	0.54	1.08	0.81	1.08	0.54	1.35	1.08	0.54	0.81	1.08	0.54	0.40
9-Nitroanthracene-d_9	[b]	[b]	[b]	[b]	0.66[c]	2.22	2.22	2.22	3.32	0.89	2.22	1.78	0.89	1.34	1.78	0.89	0.67
2-Nitrofluoranthene-d_9	0.54	1.61	0.81	1.08	0.54	0.54	1.08	0.81	1.08	0.54	1.35	1.08	0.54	0.81	1.08	0.54	0.40
1-Nitropyrene-d_9	0.66	1.99	0.99	1.32	0.66	0.66	1.32	0.99	1.32	0.66	1.65	1.32	0.66	0.99	1.32	0.66	0.50
6-Nitrochrysene-d_{11}	1.42[d]	[e]	[e]	0.71[d]	0.57[c]	0.57	0.57	0.57	0.86	0.71	1.78	1.42	0.71	1.06	1.42	0.71	0.53
6-Nitrobenzo[a]pyrene-d_{11}	1.28[d]	[e]	[e]	0.64[d]	0.64[d]	0.63	0.63	0.63	0.93	0.62	1.55	1.24	0.62	0.93	1.24	0.62	0.46
3-Nitroperylene-d_{11}	1.23[d]	[e]	[e]	0.58[d]	0.58[d]	0.51	0.51	0.51	0.76	0.51	1.28	1.02	0.51	0.76	1.02	0.51	0.38
7- + 9-Nitrobenz[a]-anthracene-d_{11}	1.18[d]	[e]	[e]	0.59[d]	0.54[c]	1.17	1.17	1.17	1.76	0.68	1.70	1.36	0.68	1.02	1.36	0.68	0.51
1,3-,1,6-,1,8-Dinitro-pyrene-d_8 mixture	1.82	5.46	2.73	3.64	1.82	1.82	3.64	2.73	3.64	1.82	4.55	3.64	1.82	2.73	3.64	1.82	1.86

[a] See Table V-10 for a complete listing of the composited samples.
[b] Not available at time of sample extraction; 220 ng added to the 10% of the normal phase HPLC fraction (22-34 min) reserved for light nitroarene and heavy PAH analysis, added just prior to GC/MS analysis.
[c] Semi-quantitative amount added after extraction, but prior to HPLC fractionation to allow identification without quantification.
[d] Not available at the time HPLC fractionation occurred. Added to the appropriate fraction after the 2nd HPLC fractionation.
[e] Not available at the time of sample work-up and analysis not attempted.

elution with n-pentane (30 mL), CH_2Cl_2 (50 mL) and CH_3OH (50 mL) was used to segregate the aliphatic hydrocarbons (eluted with n-pentane) and polar material (eluted with CH_3OH) from the PAH and nitroarenes (eluted with CH_2Cl_2). [For the Glendora samples, deactivated silica gel with n-hexane as the eluent rather than n-pentane was used (Winer et al. 1987). However, since some of the lower molecular weight PAH were partially eluted with n-hexane, but not with n-pentane, n-pentane was employed for all remaining samples]. The fraction of interest (eluted with CH_2Cl_2) was further fractionated with the HPLC system described above using a semi-preparative Altex Ultrasphere Silica column, at a flow rate of 3 mL min^{-1}.

Although we had tested our analytical procedure on the NBS Urban Particles, SRM 1649, with satisfactory results, some unexpected problems arose during the analysis of the Glendora samples and especially for the large (sixteen filters each) composite Samples #3 and #4. At the end of the work-up procedure, GC/MS/MID analysis showed that the recovery of the internal standards, 1-nitropyrene-d_9 and 2-nitrofluoranthene-d_9 was low for Samples #3 and #4. The problem was traced to the silica open-column precleaning step. Further, the recovery of the more volatile PAH internal standards, i.e., fluoranthene-d_{10} and pyrene-d_{10}, was low most likely due to excessive drying of the benzene/methanol extracts to obtain the extract weight.

To obtain results on the nitroarenes of M.W. 247 and verify the PAH results, replicate composite Samples #3A and #4A were made utilizing the two filters without inlets (from the modified Hi-Vol samplers with PUF plugs) and one additional filter (from a Hi-vol sampler with an inlet) per 12-hr period which had been reserved for another use. Thus, Samples #3A and #4A were replicates of Samples #3 and #4, respectively, except for the absence of the size cut-off inlets on most of the filters used. These replicate Samples #3A and #4A were extracted with CH_2Cl_2, since this solvent was known to provide efficient recovery of the PAH and nitroarenes [although not the azaarenes (Nielsen and Clausen 1986)].

The benzene/methanol extract weights for Samples #3 and #4 were significantly higher (even taking into account the number of filters used) than for the replicate Samples #3A and #4A, due to the higher extraction efficiency of the more polar solvent system. Although this extraction efficiency was necessary for azaarene extraction, it had caused the

problems with the open-column chromatography step. Since azaarenes were on the lists of targeted compounds, we continued to use the benzene/methanol extraction system for the remaining samples, but modified our procedure by more gentle drying of the samples and, more importantly, by utilizing two or more silica columns for the open-column chromatography step for large extraction samples.

For the Glendora samples, the following mobile phase HPLC program was employed: n-hexane/CH_2Cl_2 at 95%/5% for 10 min, then a linear gradient to 100% CH_2Cl_2 over 15 min, held at 100% CH_2Cl_2 for 10 min, followed by a linear gradient to 100% acetonitrile (CH_3CN) over 10 min and held at 100% CH_3CN for 10 min. Figure VI-2 shows HPLC profiles of the extracts of the Glendora Samples #5 (day) and #6 (night), together with the mobile phase program employed. A PAH-containing fraction was collected from 4 min to 13 min (consisting of subfractions 2-5, Figure VI-2) and a nitroarene-containing fraction from 13 to 25 min (subfractions 6-8). A dinitropyrene-containing fraction was collected from 25 to 28 min (subfraction 9) and two fractions containing more polar compounds (such as hydroxynitro-PAH) were collected from 28 to 40 min (subfractions 10-13) and from 40 to 55 min (subfractions 14-18). These latter three fractions were stored for future analyses.

The composite samples from the remaining six sites, as well as the single composited sample from San Nicolas Island, were fractionated using the same HPLC mobile phase program as for the PUF plug samples, i.e., 100% n-hexane for 10 min, then a linear gradient to 95%/5% n-hexane/CH_2Cl_2 over 5 min, followed by a linear gradient to 100% CH_2Cl_2 over 25 min, held at 100% CH_2Cl_2 for 10 min, followed by a linear gradient to 100% of CH_3CN over 10 min and held at 100% CH_3CN for 10 min. Figures VI-3 through VI-8 show the HPLC profiles of day and night composite samples collected at Yuba City, Concord, Mammoth Lakes, Oildale, Reseda and Pt. Arguello, respectively, and Figure VI-9 shows the HPLC profile of the San Nicolas Island sample. The PAH-containing fraction was collected from 7 min to 22 min (subfractions 3-7) and a nitroarene-containing fraction from 22 min to 34 min (subfractions 8-11). Subfraction 12 containing the dinitropyrenes was kept separate and the remaining more polar subfractions were composited into three fractions, 13-16, 17-19 and 20-24, which were stored for future use. The 22-34 min nitroarene fraction also contained some higher molecular weight (M.W. >252) PAH.

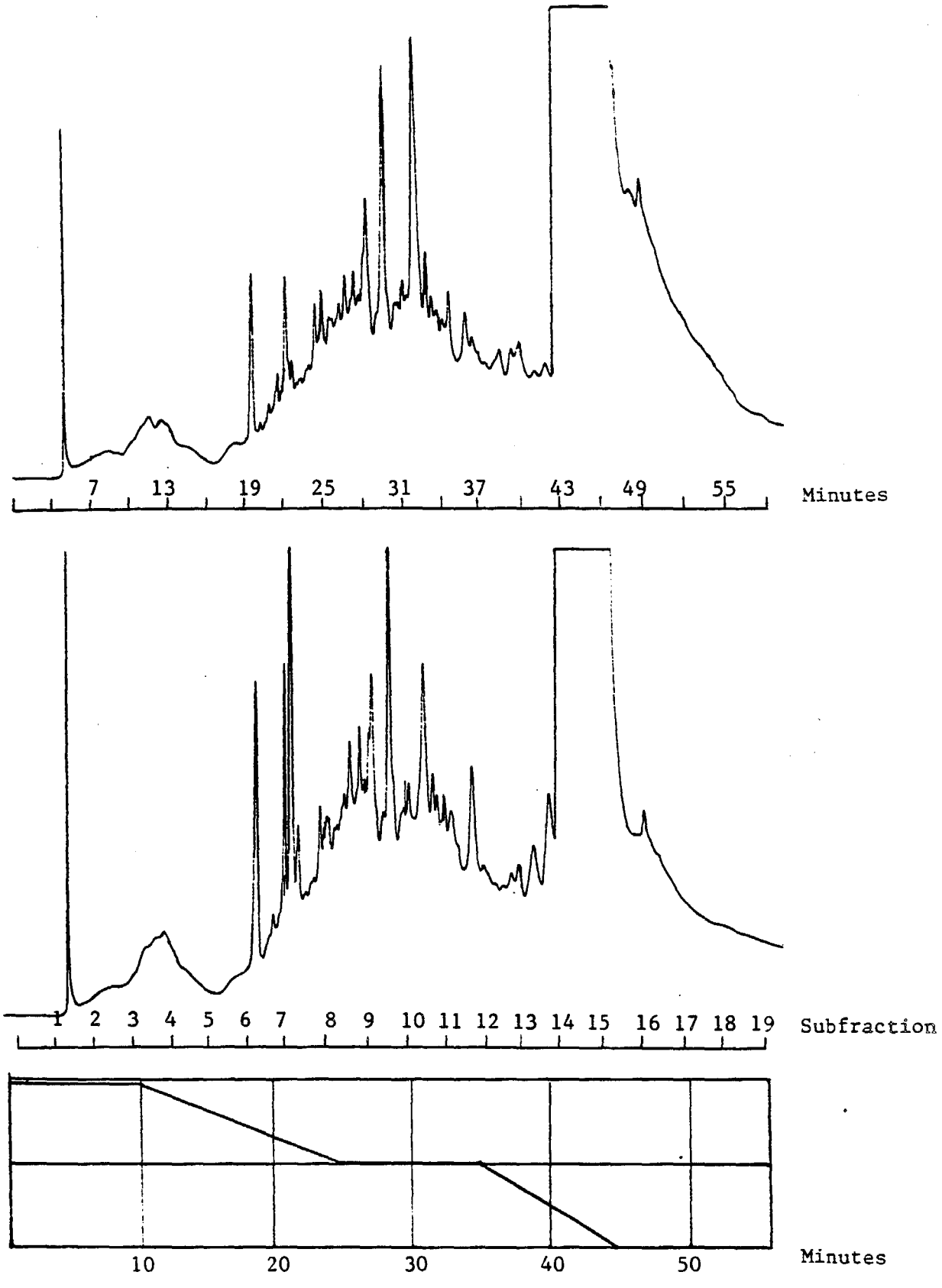


Figure VI-2. HPLC profiles (254 nm) and gradient solvent program of Glendora POM Sample #5 (day, upper trace) and #6 (night, lower trace). HPLC subfractions were combined as follows: 2-5, 6-8, 9, 10-13, 14-18.

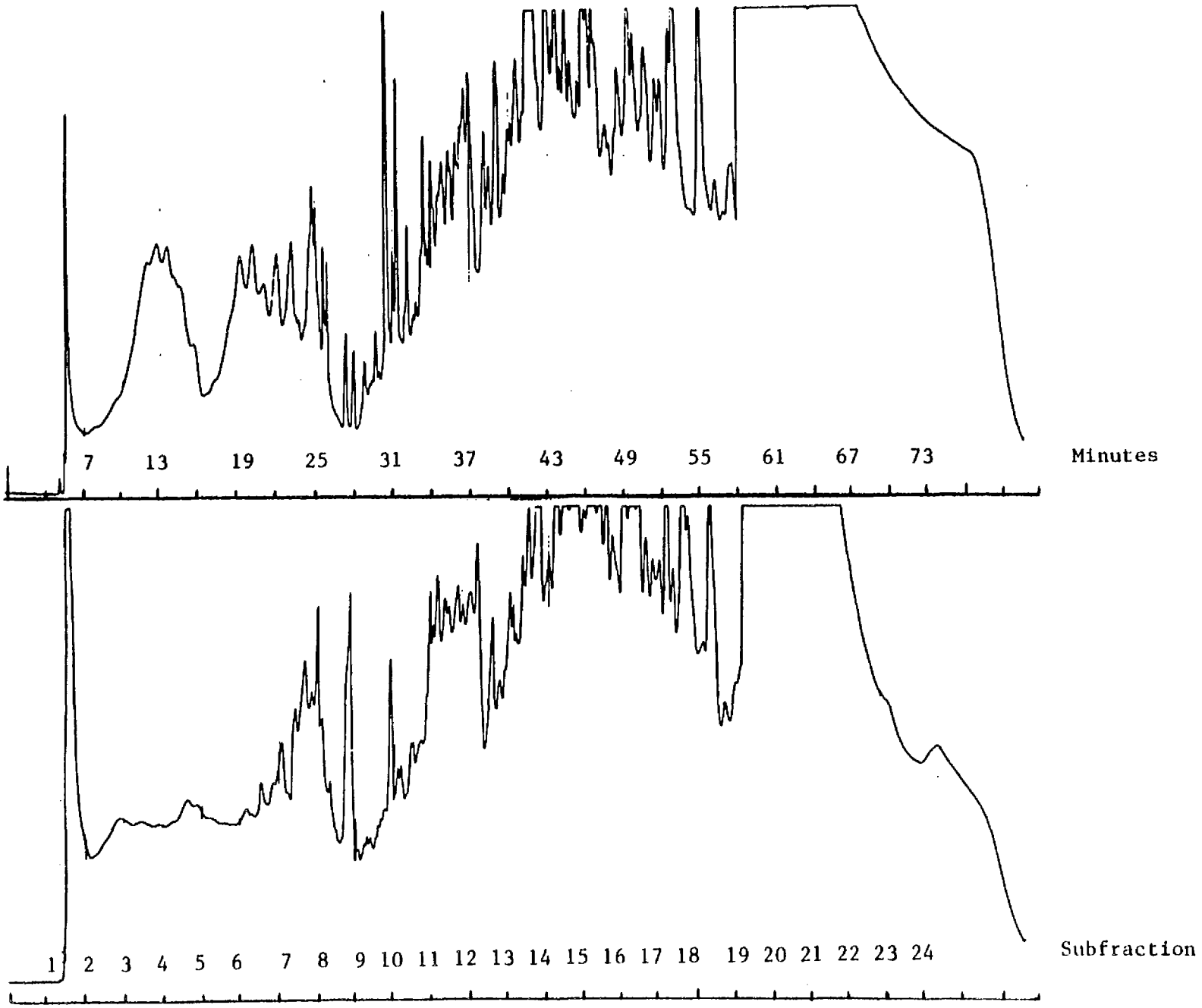


Figure VI-3. HPLC profiles (254 nm) of Yuba City POM Sample #1 (day, upper trace) and #3 (night, lower trace). HPLC subfractions were combined as follows: 3-7, 8-11, 12, 13-16, 17-19, 20-24.

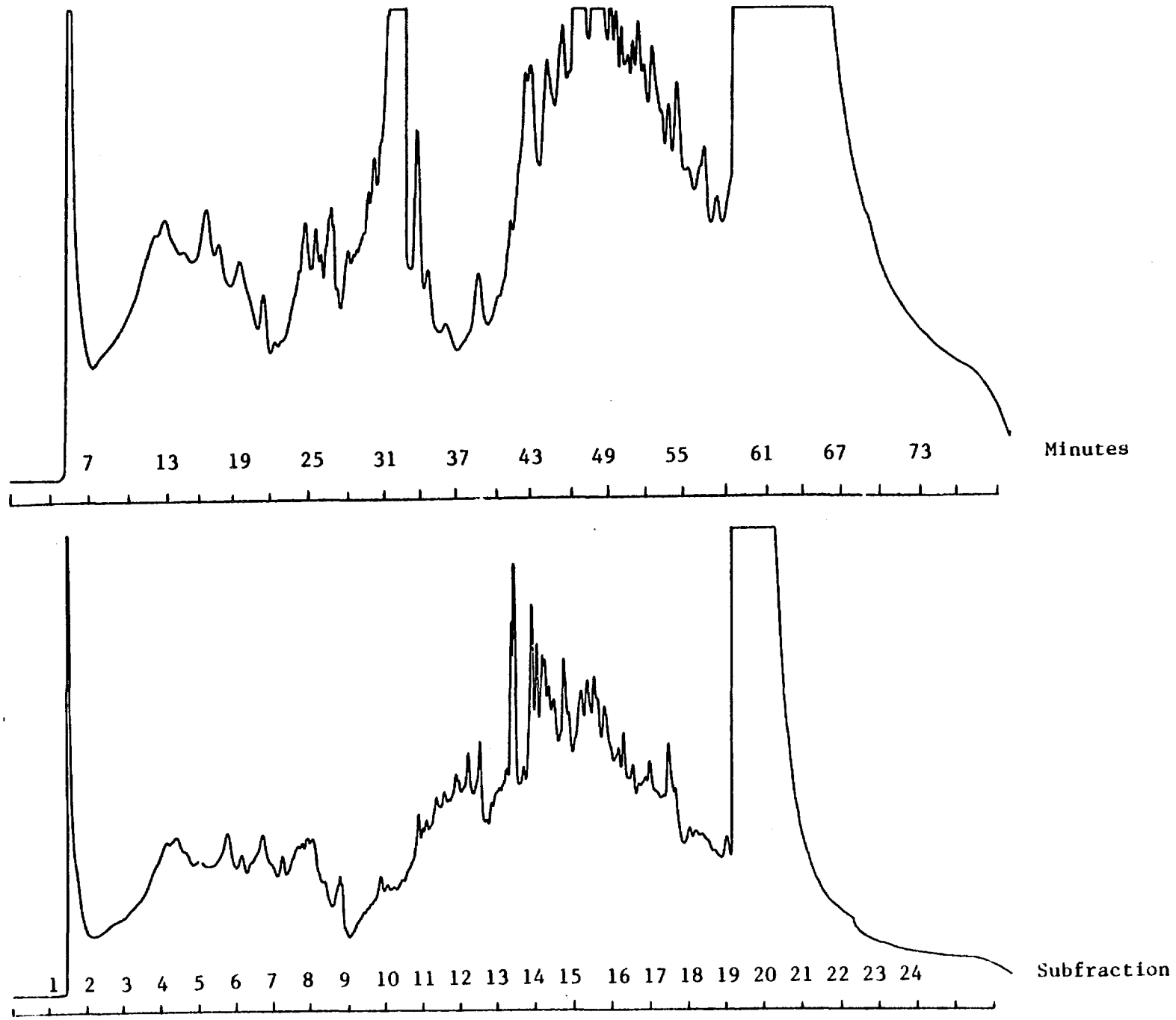


Figure VI-4. HPLC profiles (254 nm) of Concord POM Sample #1 (day, upper trace) and #5 (night, lower trace). HPLC subfractions were combined as follows: 3-7, 8-11, 12, 13-16, 17-19, 20-24.

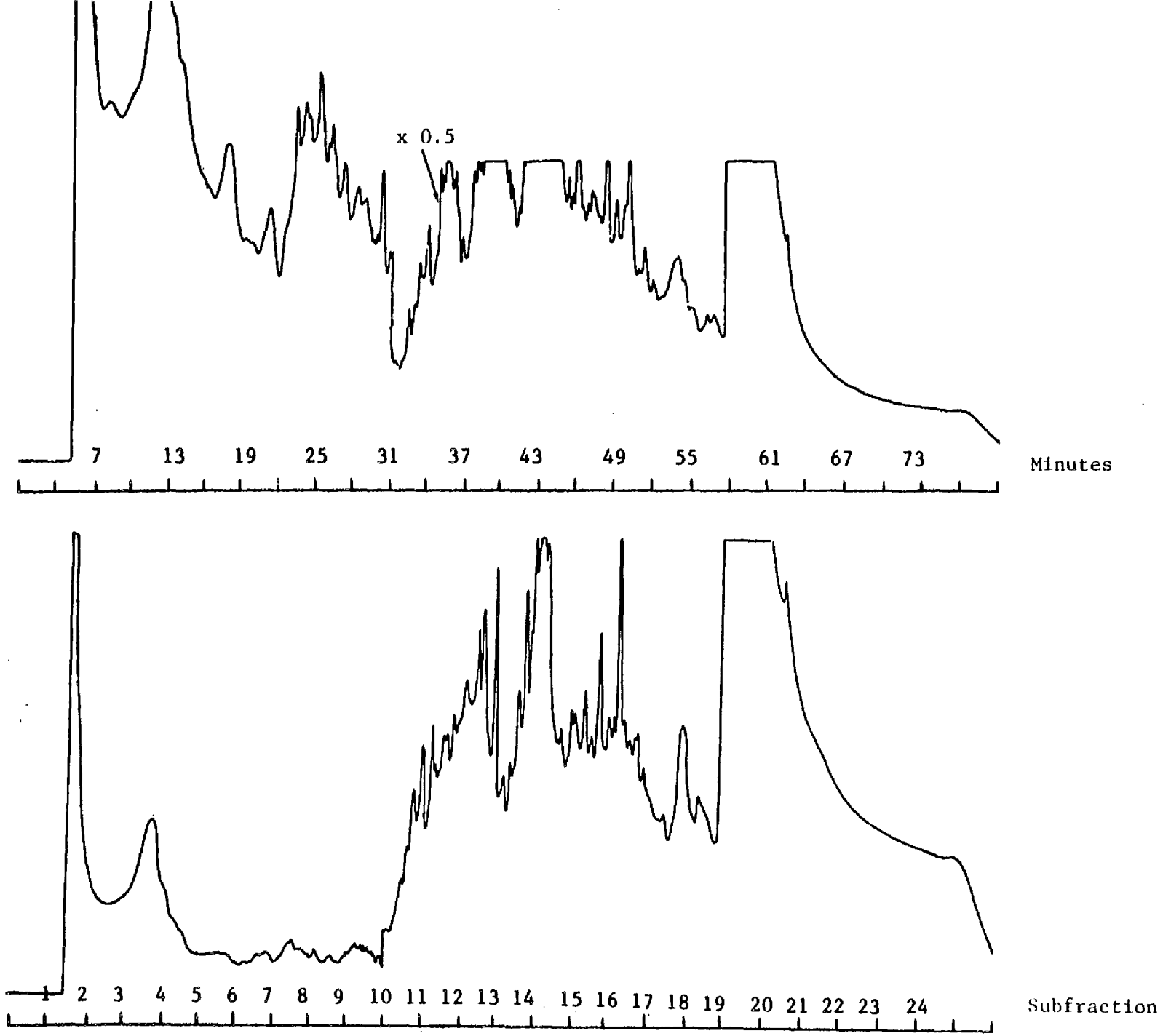


Figure VI-5. HPLC profiles (254 nm) of Mammoth Lakes POM Sample #1 (day, upper trace) and #2 (night, lower trace). HPLC subfractions were combined as follows: 3-7, 8-11, 12, 13-16, 17-19, 20-24.

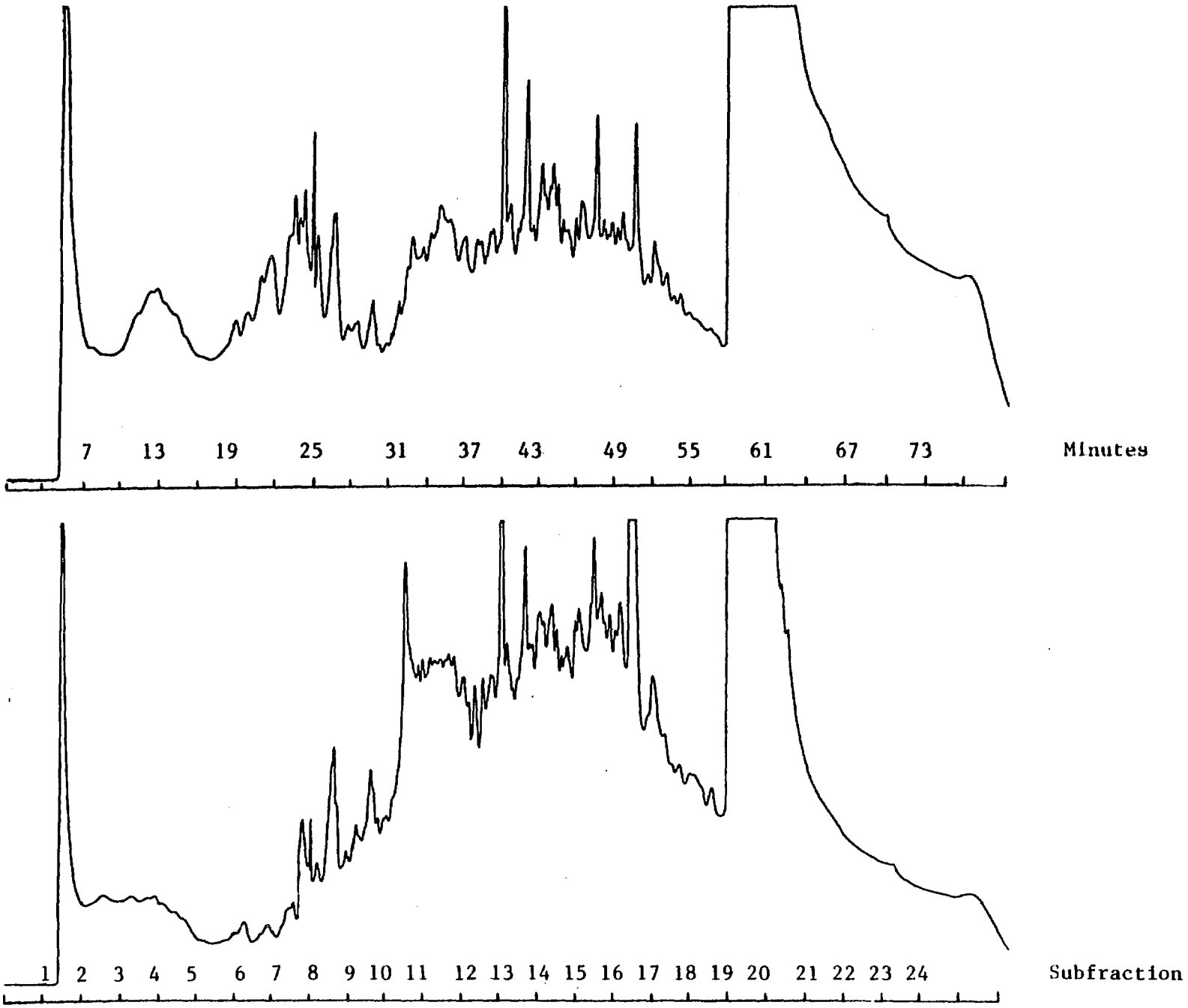


Figure VI-6. HPLC profiles (254 nm) of Oildale POM Sample #1 (day, upper trace) and #2 (night, lower trace). HPLC subfractions were combined as follows: 3-7, 8-11, 12, 13-16, 17-19, 20-24.

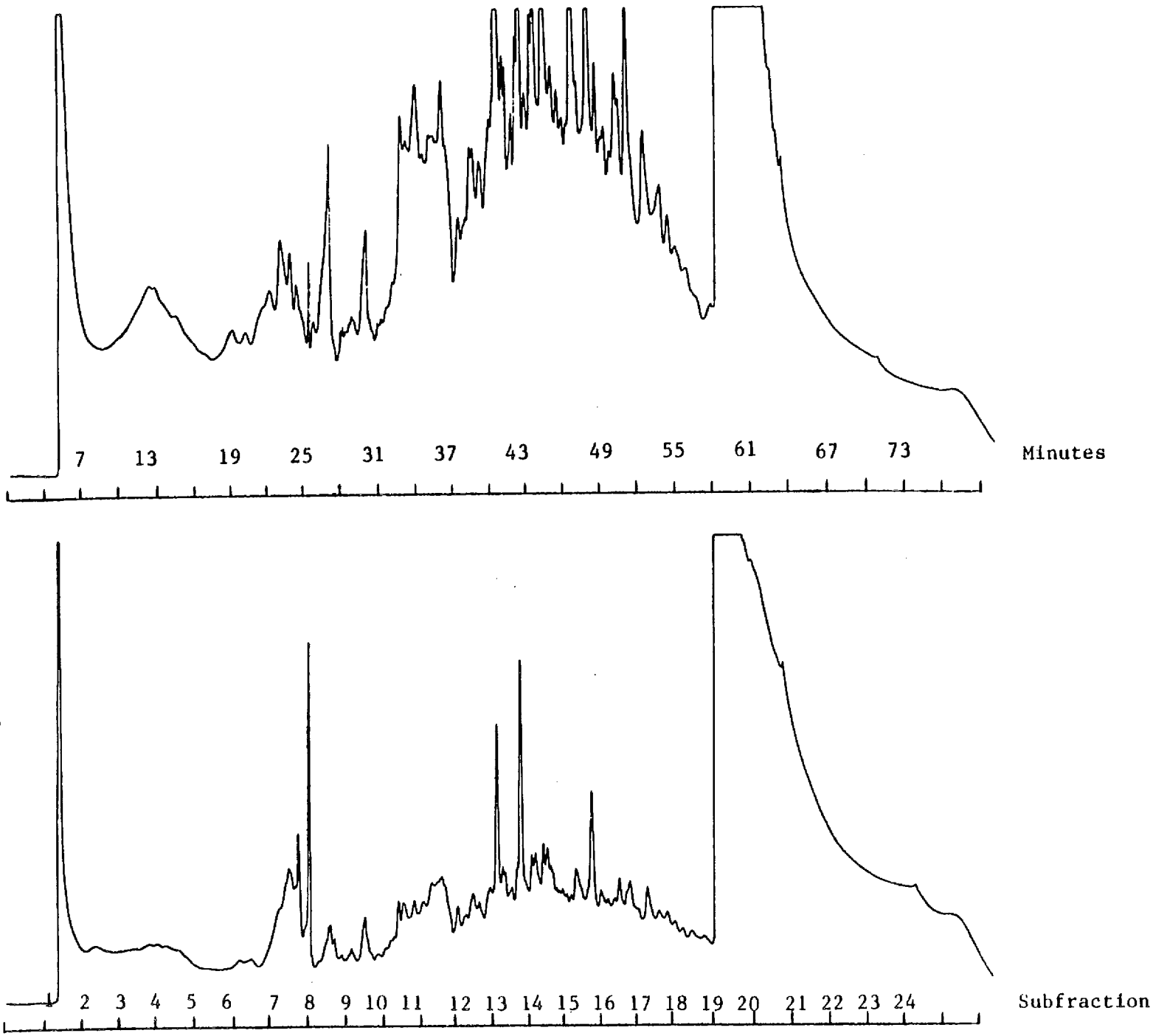


Figure VI-7. HPLC profiles (254 nm) of Reseda POM Sample #1 (day, upper trace) and #2 (night, lower trace). HPLC subfractions were combined as follows: 3-7, 8-11, 12, 13-16, 17-19, 20-24.

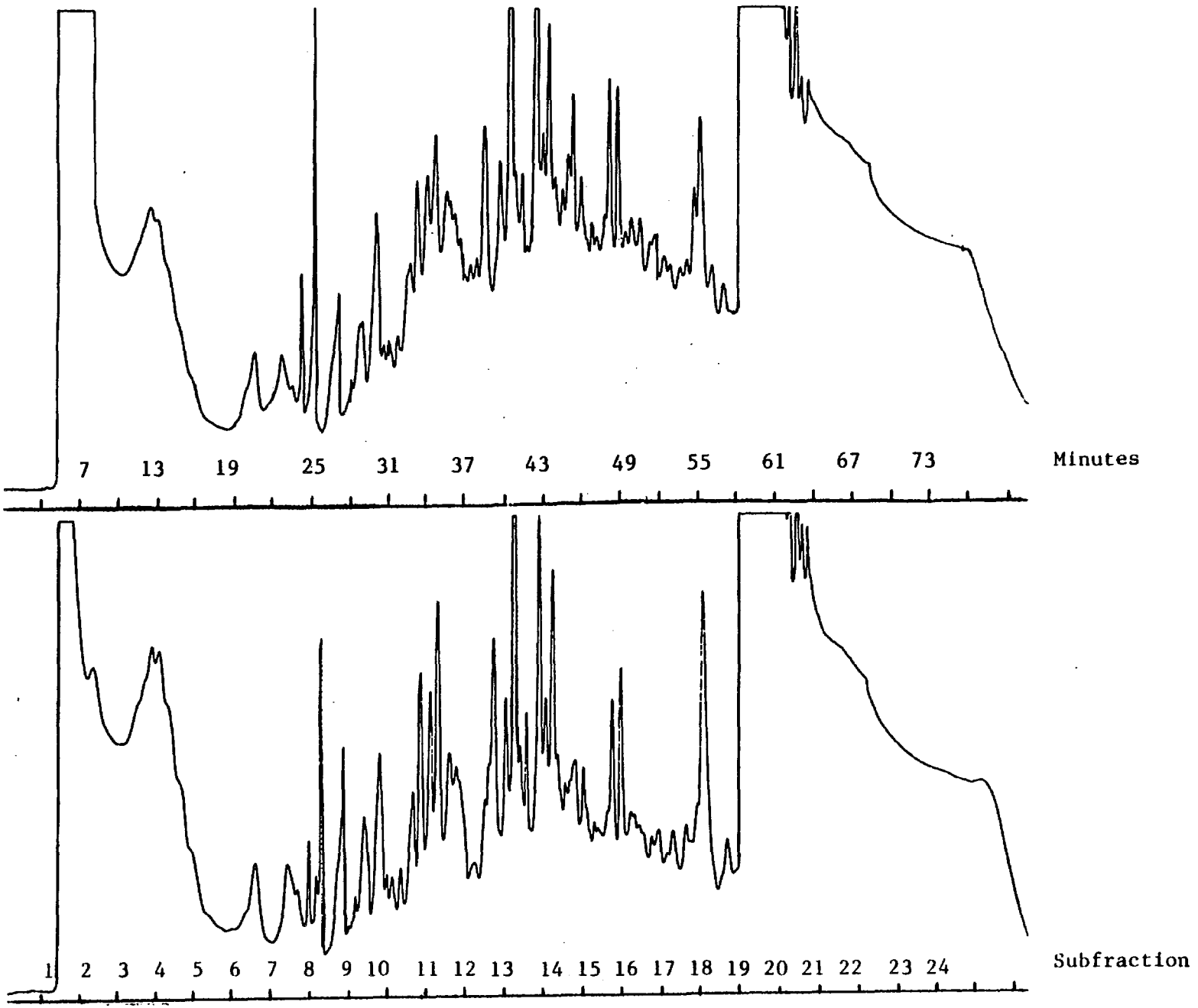


Figure VI-8. HPLC profiles (254 nm) of Pt. Arguello POM Sample #1 (day, upper trace) and #2 (night, lower trace). HPLC subfractions were combined as follows: 3-7, 8-11, 12, 13-16, 17-19, 20-24.

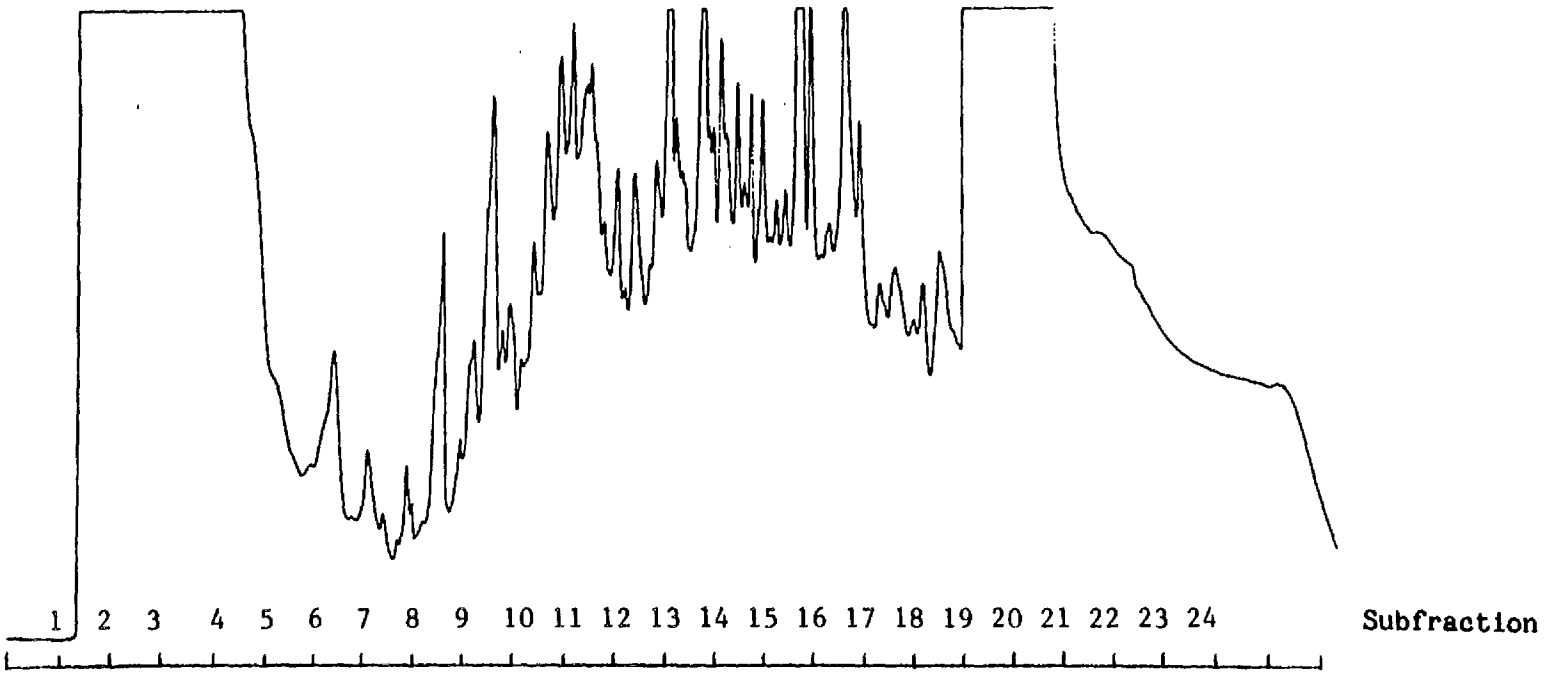


Figure VI-9. HPLC profile (254 nm) of the San Nicolas POM sample. HPLC subfractions were combined as follows: 3-7, 8-11, 12, 13-16, 17-19, 20-24.

This 22-34 min fraction was divided into two parts: 10% was analyzed by GC/MS/MID for PAH and the lower molecular weight nitroarenes and 90% was fractionated further by reverse-phase HPLC using an Altex semi-preparative Ultrasphere ODS column and a Beckman Model 334 HPLC equipped with a Beckman Model 164 uv/vis detector. The mobile phase program (using a flow rate of 3 mL min^{-1}) employed was: 80% methanol, 20% water for 35 min, then a linear gradient to 100% methanol over 5 min held at 100% methanol for 15 min. Figure VI-10 shows the reversed-phase HPLC profiles of the nitroarene-containing fractions (subfractions 8-11) from the Mammoth Lakes Sample #2 (upper trace) and the Reseda Sample #2 (lower trace). A fraction containing isomeric nitroarenes of M.W. 247 (and the deuterated internal standards, 2-nitrofluoranthene-d_9 and 1-nitropyrene-d_9) and (as discussed below) nibrobenz[a]anthracene(s) was collected from 22 min to 38 min and a fraction containing higher molecular weight nitroarenes (including 6-nitrochrysene, 3-nitroperylene and 6-nitrobenzo[a]-pyrene) from 38 to 60 min. These fractions were then analyzed by GC/MS/MID as described below.

For some samples (as can be seen from the upper trace of Figure VI-10) the two HPLC fractionations performed did not sufficiently isolate the desired nitroarenes from the other species present. For all of the Mammoth Lakes samples and for certain of the Concord samples, GC/MS quantification of the M.W. 247 nitroarenes was not possible due to the large amount of interfering compounds present. Therefore, a third HPLC fractionation was performed on the samples from these sites, using a normal-phase semi-preparative Ultrasphere Si column and isocratic elution with 75% n-hexane and 25% CH_2Cl_2 at a flow rate of 3 mL min^{-1}. The fractions collected from 11 to 14 min resulted in much cleaner samples allowing useful GC/MS analyses of the M.W. 247 nitroarenes to be carried out.

Following successful GC/MS analysis of the M.W. 247 nitroarenes, analysis of the higher M.W. nitroarenes was attempted. GC/MS/MID analysis of the 38-60 min fraction from the 2nd HPLC fractionation described above, showed that this fraction did not contain the deuterated nitrobenz[a]-anthracenes. Analysis of this fraction for 6-nitrochrysene and 6-nitrobenzo[a]pyrene was successful on the Glendora samples analyzed (Samples #1, #2, #5 and #6), but this fraction from sites such as Concord and Mammoth Lakes contained too many high M.W. PAH species to allow

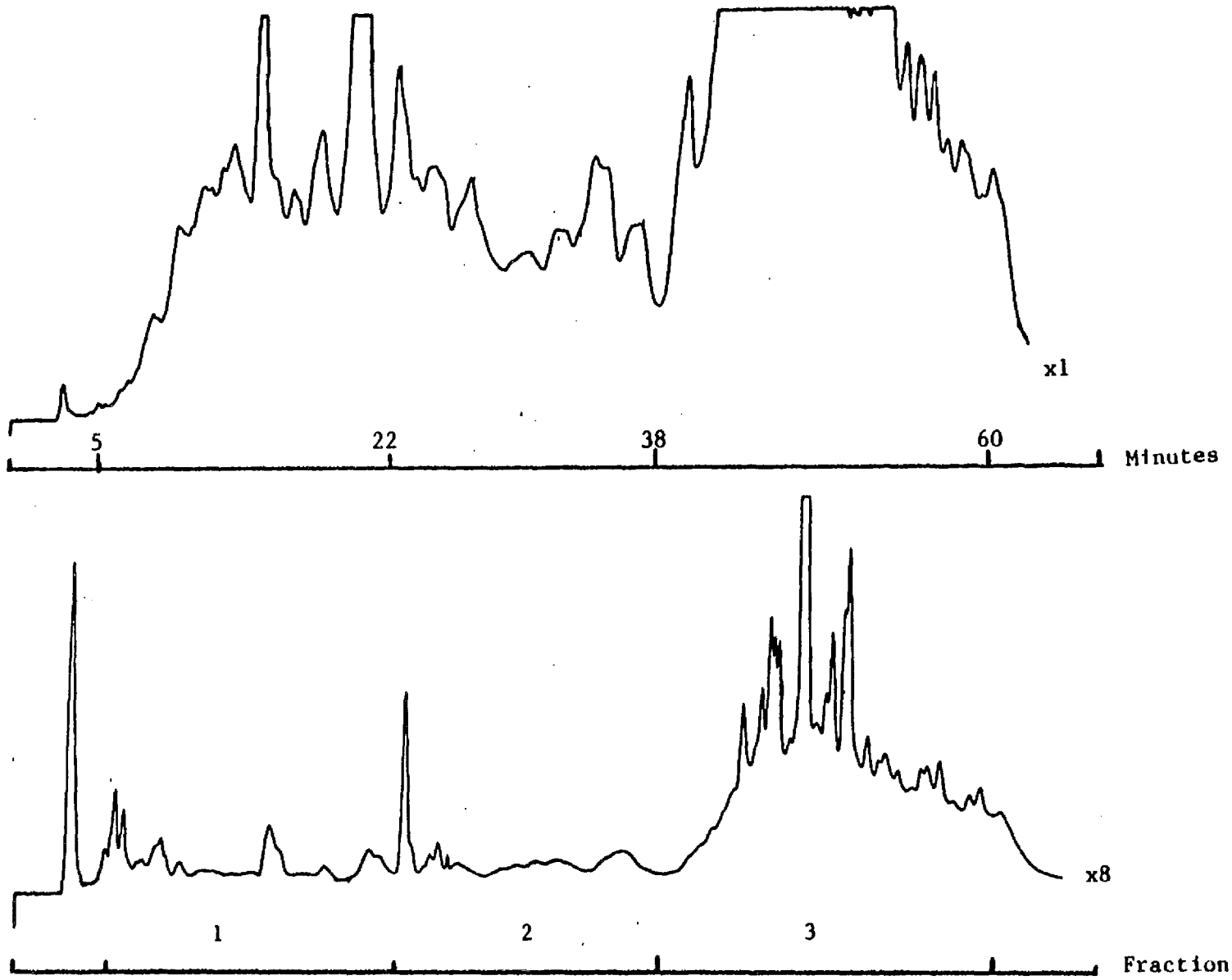


Figure VI-10. Reversed-phase HPLC profiles (254 nm) of fractions 8-11 of Mammoth Lakes Sample #2 (night, upper trace) and of Reseda Sample #2 (night, lower trace). Note that the amplification factor for the Mammoth Lakes sample is 8 times lower than that for the Reseda sample.

sufficiently sensitive GC/MS/MID analyses of the high M.W. nitroarenes which were, if present, only at much lower levels. A third HPLC fractionation (Ultrasphere Si column, 10 min at 90% hexane, 10% CH_2Cl_2; programmed over 10 min to 60% hexane, 40% CH_2Cl_2; held isocratic for 10 min; programmed over 5 min to 100% CH_2Cl_2, held for 5 min then returned to starting conditions) was carried out on selective samples followed by GC/MS/MID analysis.

The deuterated nitrobenz[a]anthracenes (and in Reseda Samples #1 and #2, also the 6-nitrochrysene-d_{11}) were found to elute in the second HPLC fractionation in the same fraction as the M.W. 247 nitroarenes. HPLC fractionation of a standard showed that for those samples subjected to a third HPLC fractionation (i.e., Concord and Mammoth Lakes) for the M.W. 247 species, the nitrobenz[a]anthracene could be expected in a different fraction from the M.W. 247 species. The appropriate fractions of samples from Glendora, Yuba City, Concord and Reseda were analyzed for nitrobenz[a]anthracenes; based on the data for the M.W. 247 nitroarenes, levels at the other sites were assumed to be low.

Azaarenes. In addition to PAH, PASH and nitroarenes, azaarenes were on our list of targeted compounds to monitor. We expended considerable effort developing a method for azaarene analysis. Glendora Samples #3 and #4 were analyzed according to our original procedure which resulted in the azaarenes being distributed between the CH_2Cl_2 and CH_3OH open-column fractions, requiring that both fractions be subjected to acid-base fractionation. After modifying our open-column pre-separation procedure, as detailed below, we were able to isolate the azaarenes in the CH_3OH fraction. Yuba City Sample #1 was analyzed with this modified procedure. Due to time and funding constraints, we have stored the CH_3OH open-column fraction from the remaining samples for future analysis.

A modified open-column procedure was tested as follows: A standard mixture of azaarenes was chromatographed by open column chromatography on silicic acid (Mallinckrodt, 100 mesh) prepared according to our original protocol, i.e., prewashed with CH_3OH then reactivated by overnight heating to 400°C and deactivated by the addition of 5% water by weight, and on silicic acid cleaned as above, but without water deactivation. Columns were prepared from the deactivated and non-deactivated silicic acid by adding 0.5 g of each silicic acid sample to 0.5 mL solutions of quinoline-

d_7 (8.8 μg mL^{-1}), acridine-d_9 (8.2 μg mL^{-1}) and benz[c]acridine (4.6 μg mL^{-1}) in CH_2Cl_2, evaporating the solvent under a stream of nitrogen and placing these silicic acid samples on the top of a column packed with 2 g of the corresponding silicic acid. The columns were then sequentially eluted with n-pentane (30 mL), CH_2Cl_2 (50 mL) and CH_3OH (50 mL). The eluates were concentrated by rotary evaporation at 30°C with a water aspirator vacuum and analyzed by GC-FID and/or GC/MS for the presence of azaarenes.

Neither pentane eluate contained azaarenes. The CH_2Cl_2 eluate from the column packed with deactivated silicic acid contained ~60% of the quinoline-d_7 and acridine-d_9 and ~80% of the benz[c]acridine. The CH_3OH fraction from the same column contained <5% of the quinoline-d_7, ~10% of the acridine-d_9 and ~5% of the benz[c]acridine. The CH_2Cl_2 fraction from the column packed with silicic acid not deactivated with water did not contain detectable amounts of the standard azaarenes. In this case, the azaarenes were eluted entirely in the CH_3OH fraction, with the recovery ranging from ~60% (quinoline-d_7) to ~80% (benz[c]acridine). The relatively low recovery of the low molecular weight azaarene was probably due to the evaporative concentration step. It was decided, therefore, that the open-column chromatography should be done on silicic acid that had not been deactivated with water (see IV-C above).

The CH_3OH fraction from the silica open-column chromatography was subjected to acid-base separation by extraction with 5% H_2SO_4, followed by titration of the extract with 40% KOH to pH 13 and recovery of the azaarenes by extraction with CH_2Cl_2 (see Scheme VI-1). To determine the optimum solvent from which to extract the basic azaarenes with aqueous 5% H_2SO_4, acid-base extractions were performed on a standard azaarene solution as follows.

The extractions were performed in 20 mL conical test tubes equipped with glass stoppers, and a Vortex mixer was used to ensure thorough mixing. Solutions, each of 4 mL volume, of standard azaarenes (quinoline-d_7, 4.4 μg, acridine-d_9, 4.1 μg, benz[c]acridine, 2.3 μg) in either CH_2Cl_2 or diethyl ether (HPLC grade, additionally precleaned by chromatography on alumina) were extracted 3 times each with 1 mL of 5% H_2SO_4 (ultrapure H_2SO_4, 96+%, Alfa Products). The combined aqueous layers from each of the solutions were adjusted to pH 13 with 40% KOH (ultrapure KOH, Alfa

Products) and extracted 3 times with 1 ml of CH_2Cl_2. The combined organic layers were washed with 1 mL of water, dried over small amounts of anhydrous Na_2SO_4 and concentrated under a stream of nitrogen to ~100 µL. A comparison of the recoveries of azaarenes from the CH_2Cl_2 and diethyl ether solution showed that the use of diethyl ether as a solvent resulted in higher recoveries of the azaarenes.

Accordingly, our modified protocol for extraction and quantification of ambient azaarenes was as follows:

1. The extract of ambient POM is prefractionated by open-column silica chromatography, using silicic acid (Mallinckrodt, 100 mesh) prewashed with CH_3OH and reactivated by heating overnight to 400°C. The column is eluted sequentially with n-pentane (30 mL), CH_2Cl_2 (50 mL) and CH_3OH (50 mL).

2. The CH_3OH fraction from this step is concentrated under vacuum and redissolved in diethyl ether.

3. An acid-base separation is carried out by extraction with 5% H_2SO_4, followed by titration of the extract with 40% KOH to pH 13 and reextraction with CH_2Cl_2.

4. The CH_2Cl_2 extract is washed with water, dried, concentrated and analyzed by GC/MS.

PAH GC/MS Analyses. PAH identifications and quantifications were made using a Hewlett Packard 5890 GC with an ~50 m 5% PhMe Silicone (Hewlett Packard) fused-silica capillary column interfaced to a Hewlett Packard 5970 MSD. The HPLC fractions analyzed for PAH were dissolved in CH_3CN or a mixture of CH_3CN and CH_2Cl_2 for injection by the 7673A Automatic Sampler in the splitless mode. The GC conditions were as follows: injection port 350°C; initial column temperature 65°C for two minutes followed by programming at 8°C min^{-1} to a final temperature of 340°C and held isothermal for ~20 min.

Only a small fraction of any PAH below molecular weight 202 was expected to be present on the filter samples and, therefore, no ions below 202 were monitored. The following molecular ions were monitored: For the PAH listed in Table II-5: m/z 202, 226, 228, 252, 276, 278, 300, and 302; for the deuterated internal standards: m/z 212 for fluoranthene-d_{10} and pyrene-d_{10}, m/z 240 for benz[a]anthracene-d_{12} and chrysene-d_{12}, m/z 264 for benzo[a]pyrene-d_{12} and perylene-d_{12}, m/z 292 for dibenz[a,h]anthra-

cene-d_{14}; for the methyl-PAH listed in Table II-6: m/z 242, 266 and 292, and for retene its molecular ion and major fragment ion of m/z 234 and 219, respectively. Identifications were based on retention time matching with authentic standards.

The higher molecular weight PAH (M.W. >252) were present partially in the HPLC PAH-fraction and partially in the nitroarene fraction (see Scheme VI-1). 10% of the nitroarene fraction was reserved to analyze these high M.W. PAH (as well as to analyze for the lower molecular weight nitroarenes). Prior to GC/MS analysis, these fractions were spiked with chrysene-d_{12} (all of the original chrysene-d_{12} spike appeared in the PAH fraction) to serve as an internal standard for quantification, since the original internal standard for the high molecular weight PAH, i.e., dibenz[a,h]anthracene-d_{14}, was split between the PAH- and nitroarene-fractions. For quantifying the high molecular weight PAH, the amounts in the two fractions (the PAH- and nitroarene-fractions) were summed (see Section VII). The ions monitored were: for the deuterated internal standards, m/z 240, 264, 292; for the PAH and methyl-PAH, m/z 252, 266, 276, 278, 292. The results of the PAH quantifications for the twenty-four composite samples from the seven sites, the San Nicolas Island sample and the Glendora replicate Samples #3A and #4A are given in Section VII, together with examples of typical traces from the GC/MS/MID analyses.

Nitroarene GC/MS Analyses. Identifications of the nitroarenes by GC/MS/MID were made on the basis of the presence of several major fragment ions as well as retention time matching. The mass spectra of standards of the identified nitroarenes are given in Appendix B. Authentic samples of all eight of the nitrofluoranthene and nitropyrene isomers were available for retention time and fragment ion abundance comparisons. Quantifications for 1-nitronaphthalene, 9-nitroanthracene, 2-nitrofluoranthene, 1-nitropyrene, 7-nitrobenz[a]anthracene and 6-nitrobenzo[a]pyrene were made by comparison with deuterated internal standards. 2-Nitropyrene and 3- and 8-nitrofluoranthene were quantified by external calibration using 1-nitropyrene-d_9 as the internal standard.

As for the PAH on the filters, the 5% PhMe Silicone capillary GC column was utilized to separate the nitroarenes which were analyzed by GC/MS/MID. Previously, we have employed cool on-column injection for nitroarene analysis (Pitts et al. 1985a). However, we found that we were

able to use splitless injection (and therefore automatic injection) if the inlet temperature was not above 300°C and the inlet liner was cleaned frequently. It was necessary to analyze several different HPLC fractions to quantify the nitroarenes present in the filter extracts. As mentioned above, the 10% of the nitroarene fraction reserved to analyze the high molecular weight PAH was also analyzed for the lower molecular weight nitroarenes which were not expected to remain after concentration of the reverse phase HPLC eluent (methanol/water). The ions monitored were as listed above (Section VI-B, page VI-6) for the nitroarenes analyzed in the PUF plug extracts. Splitless automatic injections were made with injection port at 250°C and the column at 50°C. The column was programmed at 8°C min^{-1} to 280°C, while data were collected and then programmed at 20°C min^{-1} to 330°C.

The most abundant nitroarenes we have previously observed on filter samples are the nitrofluoranthenes and nitropyrenes (M.W. 247), certain isomers of which are the result of atmospheric reactions of the parent fluoranthene and pyrene. Thus, measuring these species at all seven sites was expected to provide interesting data both on nitroarene emissions and on their atmospheric formation. As described above, the nitroarenes of M.W. 247 were isolated by normal-phase HPLC followed by reverse-phase HPLC. This procedure had worked well in the past for analyzing POM samples from Claremont and Torrance, CA. However, for two of the seven sites, Mammoth Lakes and Concord, the very high levels of high molecular weight PAH present caused interferences in the GC/MS/MID analyses and only an upper limit for the nitroarenes could be determined. A third HPLC fractionation was done for these samples (described above) and they were reanalyzed by GC/MS/MID and the nitroarenes quantified.

The fractions to be analyzed for the M.W. 247 nitroarenes were dissolved in CH_2Cl_2. The GC conditions were as follows: splitless injection with the injection port at 250°C, and the initial column temperature at 60°C. The GC was programmed at 12°C min^{-1} to 340°C and held at 340°C for approximately 10 min. The molecular ion and fragment ions monitored were: $[M]^+$, m/z 247; $[M-NO]^+$, m/z 217; $[M-NO_2]^+$, m/z 201: $[M-HNO_2]^+$, m/z 200 and $[M-NO-CO]^+$, m/z 189 and the corresponding ions for the deuterated species: m/z 256, 226, 210, 208, 198.

Analyses of the M.W. 273 and M.W. 297 nitroarenes were made as follows. The HPLC fractions were dissolved in a mixture of CH_2Cl_2 and CH_3CN and injected automatically in the splitless mode with the injection port at 300°C and the initial column temperature at 50°C. The column was then programmed at 8°C min^{-1} to 340°C. The molecular ions and fragment ions monitored for nitrobenz[a]anthracenes and nitrochrysenes were: $[M]^+$, m/z 273; $[M-NO]^+$, m/z 243; $[M-NO_2]^+$, m/z 227, $[M-HNO_2]^+$, m/z 226; $[M-NO-CO]^+$, m/z 215 and the corresponding ions for the deuterated standards at 10 or 11 amu higher. The molecular ions and fragment ions monitored for the nitrobenzo[a]pyrenes and nitroperylenes were: $[M]^+$, m/z 297; $[M-NO]^+$, m/z 267; $[M-NO_2]^+$, m/z 251; $[M-HNO_2]^+$, m/z 250; $[M-NO-CO]^+$, m/z 239 and the corresponding ions for the deuterated standards at 10 or 11 amu higher.

The concentrations of 2-nitrofluoranthene and 1- and 2-nitropyrene for the twenty-four filter composite samples from the seven sites and from San Nicolas Island are given in Section VII. Ambient concentrations of 9-nitroanthracene for the twenty-four filter composite samples and in some cases, 1- and 2-nitronaphthalene (1- and 2-nitronaphthalene were mainly observed in the PUF plug samples) are also given in Section VII together with data on the M.W. 273 and M.W. 297 nitroarenes for selected samples.

D. Chemicals

The sources of our standards for the compounds to be monitored are listed along with these compounds in Tables II-5 through II-8. The following deuterated chemicals for use as internal standards were obtained from commercial sources: phenanthrene-d_{10}, biphenyl-d_{10}, anthracene-d_{10}, pyrene-d_{10}, benzo[a]pyrene-d_{12}, benz[a]anthracene-d_{12}, perylene-d_{12}, dibenz[a,h]anthracene-d_{14}, acridine-d_9, quinoline-d_7 (Cambridge Isotope Laboratories); fluoranthene-d_{10}, carbazole-d_8 and dibenzothiophene-d_8 (MSD Isotopes Inc.); chrysene-d_{12} (ICN Biomedicals, Inc.), naphthalene-d_8 and 1-nitronaphthalene-d_7 (Aldrich Chemical Co.).

A number of chemicals which were commercially unavailable were synthesized in our laboratory. 2-Nitrofluoranthene-d_9, 2-nitrofluoranthene and 1-nitropyrene-d_9 were synthesized as described by Zielinska et al. (1986) and Pitts et al. (1985a). 9-Nitroanthracene-d_9 was obtained from the reaction of anthracene-d_{10} with N_2O_5 in CCl_4 solution according

to the method described by Zielinska et al. (1986). 6-Nitrobenzo[a]-pyrene-d_{11}, 6-nitrobenzo[a]pyrene and 3- and 5-nitroacenaphthene were synthesized as described by Pitts et al. (1984). 3-Nitroperylene-d_{11}, 3-nitroperylene, 6-nitrochrysene-d_{11}, 7-nitrobenz[a]anthracene and 7- and 9-nitrobenz[a]anthracene-d_{11} (9-nitrobenz[a]anthracene-d_{11} identification tentative) were synthesized according to methods described by Radner (1983). The mixture of 1,3-, 1,6- and 1,8-dinitropyrene, deuterated and nondeuterated, was obtained as described by Paputa-Peck et al. (1983). 2-Nitropyrene was provided by Dr. D. Schuetzle (Ford Motor Co.; Dearborn, MI) and 4-nitropyrene by Dr. A. Berg (University of Aarhus, Denmark). The 1-, 2-, 3-, 7- and 8-nitrofluoranthenes were synthesized as described previously (Ramdahl et al. 1985, Zielinska et al. 1986).

Additional standards were utilized that were not on the targeted list of PAH and nitroarenes. Acenaphthylene, acenaphthene and fluorene were additionally present in Standard Reference Material 1647, certified PAH (National Bureau of Standards). Acephenanthrylene was synthesized according to Zielinska et al. (1988b). 9-Nitroanthracene was purchased from the Aldrich Chemical Co. Methylnitronaphthalenes were obtained from the reaction of methylnaphthalenes with N_2O_5 in CCl_4 solution according to the method described by Zielinska et al. (1986). 1-Methyl-2-nitronaphthalene was obtained as described by Topsom and Vaughan (1957).