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PTEAM:
Monitoring of Phthalates and PAHS in Indoor and Outdoor Air Samples in Riverside, California

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

PTEAM: MONITORING OF PHTHALATES AND PAHS IN INDOOR AND OUTDOOR AIR SAMPLES IN RIVERSIDE, CALIFORNIA

Final Report
Volume II
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DISCLAIMER

PREFACE

This final report describes the results of implementing a field monitoring program for phthalates and PAHs in indoor and outdoor residential air samples in Riverside, California. Here we describe and discuss the survey design, survey operations, field monitoring and methods, quality assurance, and statistical analysis of phthalate and PAH chemicals in air samples. There is a companion report, Vol. 1, which presents particle, elemental and statistical analyses results. A third report will be authored by the School of Public Health at Harvard University and will discuss the modeling of indoor/outdoor/personal air relationships for aerosols and elemental data collected from Riverside, CA population.

ACKNOWLEDGMENTS

The success of this project was the product of the work and input of a number of people. The authors wish to thank all those who contributed to the design, implementation, analysis, and reporting of this study.

Overall project management was provided by Ms. Elizabeth Ota of the California Air Resources Board with the assistance of Ms. Peggy Jenkins, Manager of the Indoor Exposure Assessment Section. Mr. Dane Westerdahl was responsible for initiating this project as a collaborative effort with the U.S. EPA.

We would like to thank the Research Triangle Institute (RTI) staff members who participated in the study. They include James Beach, Linda Ellis, Brenda Hodges, Roy Whitmore and Mike Roberds. We would also like to thank all of the individuals at the U.S. EPA, RTI, Acurex, and Harvard University who were responsible for the design and implementation of the "Particle Total Exposure Assessment Methodology Study".

The authors would especially like to thank the study respondents, who graciously allowed us to enter their homes for collection of samples and information. Their participation has enabled us to conduct the study and obtain new information on indoor pollutant concentrations and exposures for PAHs and phthalates.

This report is submitted in fulfillment of California Air Resources Board Contract No. A933-144, "PTEAM: Monitoring of Phthalates and PAHs in Indoor and Outdoor Air Samples in Southern California," by Research Triangle Institute under the sponsorship of the California Air Resources Board. Work on this research project was completed as of December 1992.

ABSTRACT

The primary purpose of this study was to obtain indoor and outdoor air concentration data for benzo[a]pyrene, other polynuclear aromatic hydrocarbons (PAHs), and phthalates in California residences to be used in making exposure predictions. To meet these objectives, a field monitoring study was performed in 125 homes in Riverside, California in the Fall of 1990. In each home, two 12-hour indoor air samples were collected during daytime and overnight periods. In a subset of 65 homes, outdoor air samples were also collected. PAH and phthalate concentrations were measured in collected air samples using gas chromatography/mass spectrometry techniques. Along with field monitoring, information on potential source usage in the home was collected using questionnaires. This study was performed in conjunction with an indoor air/personal exposure monitoring study for particulates sponsored by the U. S. Environmental Protection Agency.

Prior to statistical analysis, sampling weights were developed. When the sample size was sufficiently large, these weights were applied to the field monitoring results which allowed statistical estimates to be made that represented 61,520 households in Riverside (excluding the area around March Air Force Base) with at least one nonsmoking resident over the age of 10. Mean air concentrations and concentration distributions were calculated for the target PAHs and phthalates in four sample types (indoor/daytime, indoor/nighttime, outdoor/daytime, and outdoor/nighttime). It should be emphasized that results from this study are for one city during a single season and that PAH and phthalate air concentrations and relationships may be different in different seasons and in different parts of the state.

Results showed several interesting trends for the PAHs. First, relative air concentrations for the individual PAH species in all four sample types show highest concentrations for the more volatile, 3- and 4-ringed species and lowest concentrations for the

particulate-phase 5-, 6-, and 7-ringed species. Highest median air concentrations were found for phenanthrene (8.8 to 16 ng/m^3) followed by acenaphthylene (1.8 to 6.9 ng/m^3), fluoranthene (1.6 to 2.3 ng/m^3), and pyrene (1.6 to 2.0 ng/m^3). Median concentrations for the particulate phase 5- to 7-ringed species were an order of magnitude lower with lowest median air concentrations reported for benzo[a]pyrene (0.09 to 0.20 ng/m^3) and benzo[e]pyrene (0.13 to 0.22 ng/m^3). Second, indoor air samples showed little or no increase in median or mean air concentrations compared to outdoor concentrations, although several homes did show very high PAH concentrations. Third, indoor air concentrations for most PAHs, including benzo[a]pyrene (BaP) were higher in homes where smoking took place compared to homes where there was no smoking. The maximum indoor concentration for BaP was 56 ng/m^3 compared to the maximum outdoor concentration at 2.9 ng/m^3. Finally, considerably higher nighttime concentrations were reported for outdoor samples compared to the daytime samples. For example, the median nighttime/outdoor air concentration for BaP was 0.19 ng/m^3 while the corresponding daytime concentration was less than half that value at 0.09 ng/m^3. This trend was seen for all of the particulate phase 5- to 7-ringed PAHs as well as the more volatile 3-ringed species. This effect probably resulted from photodegradation of PAHs during the day.

All of the phthalates (except di-n-octylphthalate) showed high indoor air concentrations compared to the PAHs. Diethylphthalate and di-n-butylphthalate showed the highest indoor air concentrations with median daytime concentrations of 340 and 420 ng/m^3, respectively. Median outdoor air levels for the phthalates were at least an order of magnitude lower than the corresponding indoor levels. Di-n-octylphthalate had median concentrations below the quantifiable limit (3.2 ng/m^3) for all four sample types. These data suggest that indoor phthalate concentrations arise primarily from indoor sources and that most of the exposure to airborne phthalates will occur indoors.

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GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

a	-	Air Exchange Rate
A	-	GC/MS Integrated Peak Area
AC	-	Alternating Current
ARB	-	Air Resources Board
BaP	-	Benzo[a]pyrene
BeP	-	Benzo[e]pyrene
BkF	-	Ben[k]fluoranthene
C	-	Solution Concentration
CAAQS	-	California Ambient Air Quality Standard
CATs	-	PFT Collectors
C_i	-	Indoor Concentration
C_o	-	Outdoor Concentration
C_{oi}	-	Contribution of Outdoor Pollution Levels to Indoor Concentration
db	-	Decibel
°C	-	Degree Centigrade
DEHP	-	Di-2-ethylhexylphthalate
EPA	-	U.S. Environmental Protection Agency
ETS	-	Environmental Tobacco Smoke
f	-	Fractional Penetration of Outdoor Concentration
FB	-	Field Blank
FC	-	Field Control
F_{oi}	-	Fractional Contribution of Outdoor Pollution Levels to Indoor Concentrations
FSU	-	First Stage Sampling Units
G.S.E.	-	Geometric Standard Error
GC/ECD	-	Gas Chromatography/Electron Capture
GC/MS	-	Gas Chromatography/Mass Spectrometry
h	-	Hour
HEQ	-	Household Enumeration Questionnaire
k	-	Pollutant Decay Rate

L - Liter

m/z - Mass-to-Charge Ratio

m - Air Mixing Between House Zones

m^3 - Cubic Meter

mA - Milliamp

MB - Method Blank

MC - Method Control

min - Minute

mL - Milliliter

mm - Millimeter

Mn_{10} - Manganese Associated with Inhalable Particulate

$Mn_{2.5}$ - Manganese Associated with Respirable Particulate

MQL - Method Quantifiable Limit

MS - Mass Spectrometry

n - Number of Observations

NAAQS - National Ambient Air Quality Standard

NE - Northeast

ng - Nanogram

NIST - National Institute of Standards and Technology

NQ - Below the Method Quantifiable Limit

NW - Northwest

PAH - Polynuclear Aromatic Hydrocarbon

Pb_{10} - Lead Associated with Inhalable Particulate

$Pb_{2.5}$ - Lead Associated with Respirable Particulate

PEM - Personal Exposure Monitor

PFT - Perfluorotracer

PM_{10} - Respirable Particulate

$PM_{2.5}$ - Inhalable Particulate

PTEAM - Particle Total Exposure Assessment Methodology

QC - Quality Control

QL - Quantitation Limits

% RMD - % Relative Mean Deviation

RRF	-	Relative Response Factor
% RSD	-	Percent Relative Standard Deviation
RTI	-	Research Triangle Institute
S.D.	-	Standard Deviation
S.E.	-	Standard Error
SAM	-	Stationary Outdoor Monitor
SE	-	Southeast
SIM	-	Selected Ion Monitoring
SIM	-	Stationary Indoor Monitor
SRM	-	Standard Reference Material
ss	-	Source Strength
SSI	-	Size Selective Inlet
Std	-	External Quantitation Standard
t	-	Analyte
T	-	Analyte Amount in Sample Extract
$t_{0.99}$	-	Students One-tailed t Statistic at the 99% confidence Level with Seven Degrees of Freedom
TAC	-	Toxic Air Contaminant
TEAM	-	Total Exposure Assessment Methodology
µg	-	Microgram
µL	-	Microliter
µm	-	Micron
v	-	House Volume
V	-	Volt
Ve	-	Extract Volume
XRF	-	X-ray Fluoresence

SECTION 1

INTRODUCTION AND STUDY DESIGN

Section 39660.5 of the California Health and Safety Codes requires the Air Resources Board (ARB) to assess indoor exposure to substances being considered for identification as toxic air contaminants (TACs). Benzo[a]pyrene (BaP) is a carcinogen and di-2-ethylhexylphthalate (DEHP) is a teratogen that are currently under consideration. Other polynuclear aromatic hydrocarbons (PAHs) are scheduled for future consideration. The primary objective of this research study was therefore to obtain residential indoor air concentration data on BaP and DEHP so that reasonable exposure predictions can be made for California residents. Data on air concentrations of the other PAHs and phthalates listed in Table 1-1 were also generated during this study. Simultaneous measurement of outdoor air concentrations were made in approximately half of the homes to investigate the relationship between indoor and outdoor air concentrations and to determine if chemical exposures were primarily from indoor or outdoor sources. Additional objectives were to evaluate the relationships between pollutants, potential sources, and activities. Specific project objectives are outlined in Table 1-2.

Polynuclear aromatic hydrocarbons were selected for monitoring because they are toxic air pollutants with BaP currently under consideration as a TAC. Polynuclear aromatic hydrocarbons result from combustion processes and, as such, have a number of sources. Potential indoor sources include smoking, woodburning, and grilling or frying of food. The most common outdoor source is automobile exhaust. Many of the individual PAHs, including benzo[a]pyrene, are demonstrated carcinogens or mutagens. Because PAHs are usually present in air samples at very low levels, sophisticated and expensive monitoring methods are required and, as a consequence, only a few monitoring studies on a small

TABLE 1-1. TARGET CHEMICALS

Chemical Class	Compound
PAHs	
3-Rings	Acenaphthylene
	Phenanthrene
	Anthracene
4-Rings	Fluoranthene
	Pyrene
	Benzo[a]anthracene
	Chrysene
5-Rings	Benzo[k]fluoranthene
	Benzo[a]pyrene
	Benzo[e]pyrene
6-Rings	Indeno[1,2,3-cd]pyrene
	Benzo[ghi]perylene
7-Rings	Coronene
PHTHALATES	Diethylphthalate
	Di-n-butylphthalate
	n-Butylbenzylphthalate
	Di-2-ethylhexylphthalate
	Di-n-octylphthalate

TABLE 1-2. ARB OBJECTIVES FOR THE CHEMICAL CHARACTERIZATION STUDY

1. To estimate frequency distributions for residential indoor concentrations of PAHs and phthalates in the selected study area during a single season (Fall, 1990).
2. To estimate frequency distributions for residential outdoor concentrations of PAHs and phthalates in the selected study area during a single season (Fall, 1990).
3. To evaluate whether PAH and phthalates exposures are principally from indoor or outdoor microenvironments in the selected study area during a single season (Fall, 1990).
4. To estimate the contribution of outdoor levels of PAHs and phthalates to indoor levels in the selected study area during a single season (Fall, 1990).
5. To correlate PAH and phthalate concentration values with other pollutant data collected on PTEAM.
6. To investigate the possible sources and activities contributing to residential indoor levels of PAHs and phthalates in the selected study area during a single season (Fall, 1990).
7. To examine the contribution of environmental tobacco smoke to indoor levels of PAHs and phthalates for the selected study area during that season.

number of homes have been performed. The most extensive monitoring data are available for BaP. BaP concentrations in restaurants (2.8-760 ng/m^3) (1-3), homes with smokers (3-5 ng/m^3) (4,5), homes without smokers (<1 ng/m^3) (1-4), and outdoors (<1 ng/m^3) (4-6) have generally been attributed to the presence or absence of smoking or other combustion sources during the monitoring period. The specific PAHs in Table 1 were selected as representative 3-, 4-, 5-, 6-, and 7-ring species. These were also the isomers detected by Wilson and Chuang during their studies on PAHs in homes with and without smokers (5).

Phthalates are commonly used plasticizers which are widespread environmental contaminants. Phthalates are routinely found in soil and waste samples. As for the PAHs, little air monitoring has been performed for these compounds. Outdoor air concentrations ranging from 0.5 to 74 ng/m^3 have been reported for di-n-butylphthalate at both rural and industrial sites throughout the world (7-10). Diethylphthalate has been reported in outdoor samples at levels ranging from 0.5 to 5.9 ng/m^3 (7-10). n-Butylbenzylphthalate and di-2-ethylhexylphthalate have been detected but not quantitated in outdoor samples (11). Very high concentrations (1.22 μg/m^3) of di-n-butylphthalate have been detected in ship quarters furnished with polyvinyl chloride tile (12).

Over the past several years, concerns have been raised over the health effects of phthalates because several have been shown to be weak mutagens. n-Butylbenzylphthalate and di-2-ethylhexylphthalate have also been demonstrated as strong teratogens in rats (13). The phthalates selected for this study are the most common plasticizers and have been routinely identified in other environmental and biological matrices (14). In addition, all phthalates selected for monitoring are listed as the U.S. Environmental Protection Agency (EPA) priority pollutants and are included on the list of hazardous substances generated by EPA's Office of Solid Waste (15).

To meet the specific project objectives, a single season field monitoring program for the PAHs and phthalates was performed in the fall of 1990. Monitoring was performed in approximately 125 homes from Riverside, California. A stratified three stage sample design was used to select a probability sample of homes for indoor microenvironmental air monitoring. A subsample of approximately 65 homes was selected for concurrent outdoor air monitoring. Field interviews were used to survey homes in the study area and enlist participation of the households selected for monitoring.

For each household, monitoring was performed over two consecutive 12-hour periods with an initial visit 24 hours prior to monitoring to install emitters for air exchange measurements and to obtain written informed consent from the study participants. At each home, indoor microenvironmental air samples were collected for PAHs and phthalates. Air exchange measurements were made using a perfluorocarbon tracer (PFT) technique. Outdoor microenvironmental measurements were performed in a subset of the study homes. At the end of each 12-hour chemical monitoring period, information was collected on the use of combustion sources during the monitoring period and the activities of residents that may have affected indoor or outdoor concentrations of PAHs and phthalates during the monitoring period.

Monitoring methods are summarized in Table 1-3. Once air samples for PAHs and phthalates were collected they were shipped back to Research Triangle Institute (RTI) for extraction and analysis. Samples for air exchange rate measurements were shipped to Harvard University for analysis.

This chemical characterization study for PAHs and phthalates was performed as a substudy in conjunction with the EPA Particle Total Exposure Assessment Methodology

TABLE 1-3. SAMPLING AND ANALYSIS METHODS

PAHs

- Particulate PAHs collected on quartz fiber filter with backup XAD-2 cartridge to collect vapor-phase PAHs.
- Collected using 115-V AC powered medium-volume (~17 L/min) pumps.
- Filters and XAD-2 extracted together by sonication using methylene chloride; extract concentrated to 0.1 mL.
- Extract analyzed by liquid injection onto a capillary gas chromatography (GC) column with electron ionization mass spectrometry (MS) in the selected ion monitoring mode.

Air Exchange

- Materials and method supplied by Harvard University.
- Perfluorocarbon tracer gas released into home at a known rate.
- Perfluorocarbon tracer gas collected on Ambersorb sorbent in capillary diffusion tube.
- Analysis by thermal desorption to a packed gas chromatography column with electron capture detection.

(PTEAM) pilot study. The overall objective of the PTEAM main study was to estimate frequency distributions of human exposure to airborne particles with the primary focus on PM_{10}. Prior to initiating this joint effort, a prepilot study was performed that served as the basis for the study design, monitoring regime, and sampling and analysis procedures (16, 17).

Although the contaminants of interest for the PTEAM main study were different than in this substudy, the study population could be used for monitoring other pollutants. Under these conditions, a joint effort with EPA became an efficient vehicle for obtaining PAH and phthalate air concentration data for homes in California.

The basic design for the PTEAM main study followed the same sequence of activities as other TEAM studies including the use of a probability sample of individuals and homes that allows results to be extended to the general population under study. For the PTEAM study, 185 individual homes were selected from Riverside, California for monitoring. Riverside was specifically chosen because it was known to have highly variable outdoor particulate concentrations and because the socioeconomic characteristics of the community appeared to provide a reasonably representative microcosm of the southern California population.

The 125 homes used in this part of the study were a subset of the 185 homes used in the PTEAM study. Field monitoring was performed in the same homes at the same time. Data generated from both parts of the study were then merged into a single data set and the statistical analyses presented in this report include information gathered from both parts of the study.

Aspects of the PTEAM main study are detailed in Volume 1 and include

- sample design and selection,
- questionnaire development,
- questionnaire administration,

- monitoring for PM_{10} and $PM_{2.5}$,
- monitoring for metals and ionic species,
- air exchange measurements, and
- data analyses associated with the above monitoring.

This substudy is described in Volume 2 and was used to monitor PAHs and phthalates in residential indoor and outdoor microenvironments. Data analysis that was specifically directed at the study objectives listed in Table 1-2 was then performed as part of this study.

The remainder of this report describes in detail the methods that were used for field sampling and analysis. Monitoring results and statistical analyses of the data are then given. Most importantly, we have provided the conclusions drawn from this study and have made recommendations for method improvements, as well as additional information that should be collected to understand exposure to PAHs and phthalates in the indoor environment. Because the PTEAM main study is such an integral part of the work performed here, it is summarized in a separate section. Where applicable, information on the PTEAM main activities is also provided in the technical sections to further elucidate the overall study design and its implementation.

SECTION 2

SUMMARY AND CONCLUSIONS

The purpose of this substudy was to obtain indoor and outdoor air concentration data for benzo[a]pyrene, other polynuclear aromatic hydrocarbons, and phthalates in California residences to be used in making exposure predictions. Additional objectives were to explore the relationships among the compounds, to determine if the compounds were principally from indoor or outdoor sources and to investigate the relationships between compounds and different types of indoor combustion sources.

To meet these objectives, a field monitoring study was performed on 125 homes in Riverside, California in the Fall of 1990. In each home, two 12-hour indoor air samples were collected during daytime and overnight periods. In a subset of approximately 65 homes, concurrent outdoor air samples were also collected. PAH and phthalate concentrations were measured in collected air samples using previously developed techniques.

This substudy was performed as part of the PTEAM main study. Data were collected from a probability sample of homes in southern California allowing concentration estimates to be made that represent 61,520 households in Riverside (excluding the area around March Air Force Base) with at least one nonsmoking resident over the age of 10. Field monitoring for PAHs and phthalates was performed at the same time in a subset of 125 homes monitored as part of the PTEAM main study. All data was merged into a single data set and statistical analyses included information gathered from both parts of the study.

Prior to statistical analysis, sampling weights were developed. When the sample size was sufficiently large, these weights were applied to the field monitoring results which allowed population estimates to be made for the resulting statistics. Several types of statistical analyses were performed on these data to meet the specific study objective.

The remainder of this section summarizes performance information on the methods that were used to conduct this chemical characterization study. The results of data analyses and conclusions are then presented as they relate to specific study objectives.

2.1 SAMPLING AND ANALYSIS METHODS

The sampling and analysis method used for PAHs and phthalates was based on methods used previously by RTI. Combined particulate and vapor-phase PAHs and phthalates were collected using medium-volume constant flow pumps (Esoteric, Model SP-2511), coupled to a sampling cartridge containing a 21 mm quartz fiber filter backed by a 4.5 g bed of XAD-2 resin. Twelve-hour samples were collected at a flow rate of ~17 L/min to provide a sample volume of 12.2 m^3. PAHs and phthalates were recovered from the combined cartridge material by sonication extraction with methylene chloride. Sample extracts were concentrated to 0.1 mL, then analyzed by gas chromatography/mass spectrometry in the selected ion monitoring mode.

Sample collection procedures worked well in the field. The monitors were small, compact, and easy to transport and set up at both indoor and outdoor sample locations. In addition, the noise levels produced by the pumps were very low, making them ideal for indoor monitors. Measured flow rate variability was less than 0.5 L/min for nominal sample flow rates of 17 L/min. The pumps were very reliable except in certain cases where the incoming line voltage to the pump dropped substantially. Taking into account all reasons for losses, 89% of the scheduled indoor samples and 73% of the scheduled outdoor air samples were collected for at least eight hours during the 12-hour monitoring period.

Several types of quality control samples were prepared and analyzed to evaluate overall method performance.

- Field controls were cartridges spiked with target analytes at known concentrations. These samples were taken to the field and treated exactly as field samples, but were not exposed.
- Field blanks were unspiked cartridges. These samples were taken to the field and treated exactly as field samples, but were not exposed.
- Filter controls were filters embedded with a known concentration of NIST urban dust certified for PAH concentrations. These samples remained in the laboratory, then were processed and analyzed with the field samples.
- Method controls were extraction solvent spiked with target analytes that were processed and analyzed with the field samples.
- Method blanks were unspiked extraction solvent that were processed and analyzed with the field samples.
- Duplicates were field samples collected at the same time and location, then processed and analyzed separately to assess precision.

Table 2-1 summarizes method performance data for all of the PAHs and phthalates measured in this study. Field and methods blanks were used to assess background contamination. Data show low levels of PAHs for all blanks indicating that background contamination was not a problem. The highest amounts were found for the low molecular weight PAHs; but these levels are low compared to the levels measured in air samples. For

TABLE 2-1. QUALITY CONTROL RESULTS FOR PAH AND PHTHALATE ANALYSES

			Mean Amount (ng)		% Recovery		
Compound	MQL[a] (ng/m^3)	Precision (Median % RMD)[b]	Method Blank (n=16)[c]	Field Blanks (n=14)	Method Controls (n=25)	Field Controls (n=14)	SRM[d] (n=6)
PAHs							
Acenaphthylene	1.0	8.7	ND[e]	1.2 ± 4.8	84 ± 11	86 ± 15	-[f]
Phenanthrene	2.8	6.1	2.1 ± 1.1	9.4 ± 13	90 ± 14	86 ± 8	-
Anthracene	0.18	7.6	ND	0.0 ± 0.0	71 ± 25	75 ± 25	-
Fluoranthene	1.1	4.4	0.3 ± 0.2	1.7 ± 4.9	104 ± 15	95 ± 10	72 ± 14
Pyrene	0.57	5.6	0.3 ± 0.9	1.5 ± 2.6	102 ± 13	96 ± 22	-
Benzo[a]anthracene	0.11	10	ND	0.1 ± 0.3	93 ± 15	83 ± 16	61 ± 09
Chrysene	0.090	8.3	ND	0.1 ± 0.3	100 ± 16	81 ± 11	-
Benzo[k]fluoranthene	0.080	6.8	ND	0.1 ± 0.4	111 ± 13	NA[g]	-
Benzo[e]pyrene	0.080	3.5	ND	0.0 ± 0.1	90 ± 10	NA	-
Benzo[a]pyrene	0.080	3.0	ND	0.0 ± 0.1	95 ± 19	NA	91 ± 17
Indeno[1,2,3-cd]pyrene	0.22	10	0.1 ± 0.4	0.1 ± 0.3	119 ± 29	NA	126 ± 33
Benzo[ghi]perylene	0.15	8.6	0.5 ± 0.8	0.2 ± 0.7	101 ± 19	NA	108 ± 09
Coronene	0.24	10	0.5 ± 1.0	0.2 ± 0.5	99 ± 30	NA	-
Phthalates							
Diethylphthalate	80	10	220 ± 330	266 ± 368	56 ± 44	65 ± 66	-
Di-n-butylphthalate	14	3.9	100 ± 53	110 ± 66	113 ± 26	110 ± 39	-
Butylbenzylphthalate	5.1	4.8	9.1 ± 6.8	15 ± 14	90 ± 25	80 ± 26	-
Di-n-octylphthalate	3.2	17	2.6 ± 3.5	8.2 ± 1.5	105 ± 27	87 ± 17	-
Di-2-ethylhexylphthalate	24	7.3	64 ± 29	94 ± 78	76 ± 24	81 ± 75	-

[a] Median method quantifiable limit.

[b]

$$\%RMD = \frac{|C_s - C_b|}{(C_s + C_b)/2} \times 100\%$$

where C_s and C_b are the measured concentrations in the field sample and the duplicate sample, respectively.

[c] Number of samples.

[d] National Institute of Standards and Technology - Standard Reference Material 1649.

[e] No instrumental response.

[f] No certified value.

[g] Not analyzed, method for field control preparation was unacceptable.

the phthalates, rather high amounts of diethyl-, di-n-butyl-, and di-2-ethylhexylphthalate were found on blank samples with slightly higher amounts found on field blanks. The highest amounts were reported for diethylphthalate with 266 ± 368 ng found on field blanks. Although amounts found in both the method blanks and field blanks were higher for the phthalates than for the PAHs, they were still lower than amounts found in indoor air samples.

Accuracy of the monitoring method for PAHs was evaluated using control samples spiked with standard solutions and NIST certified urban dust samples. During this study, it became apparent that suitable field controls were not available for the higher molecular weight, particle-bound PAHs, including BaP. Target PAHs spiked directly onto the XAD resin are not representative of chemicals on particles collected on the filter. Likewise, PAHs spiked directly onto the filter are subject to volatilization and degradation losses that would not be encountered when the chemical is attached to particles on the filter. To overcome this problem, we investigated using filters embedded with NIST certified urban dust as laboratory control samples that would mimic the behavior of particle-bound PAHs.

PAHs spiked onto XAD cartridges showed mean recoveries greater than 70% recovery for all target chemicals. Similar recoveries were also achieved from NIST certified urban particulate, although rather high recoveries were measured for indeno[1,2,3-cd]pyrene (126%). For both types of control samples, BaP gave recovery greater than 90%. Recovery of the phthalates from the field controls was more variable than for the PAHs. This was most apparent for diethylphthalate, di-n-butylphthalate, and di-2-ethylhexylphthalate. These results are probably a result of high and variable background present in the field controls. The spiking levels for these chemicals were close to the calculated quantitation limit, thus higher variability would be expected. Again, the spiking levels for the controls are substantially lower than the levels actually found in indoor air samples.

Accuracy of the monitoring methods was also evaluated by spiking each field and quality control sample with deuterated surrogate standards prior to extraction. Essentially, these surrogates represent the range of target chemicals and were designed to monitor performance of the extraction and analysis procedure in each sample. Data in Table 2-2 show acceptable recovery (mean recovery > 85%) for all four surrogate standards. Benzo[e]pyrene-d_{12} is a 5-ringed PAH that should effectively mimic the behavior of BaP during extraction and analysis. Results for this chemical showed recoveries of 89 ± 23% for analyses performed during the pilot study.

Method precision has been estimated based on results of duplicate sample pairs. Results show median relative mean deviations (% RMD) ranging from 3.0% for benzo[a]pyrene to 17% for di-n-octylphthalate between duplicate sample pairs with measurable concentrations.

Finally, method quantifiable limits (MQLs) were estimated for target chemicals as part of this study. Where feasible, MQLs were calculated based on the measurement variability of replicate samples containing low levels of target PAHs. For a number of chemicals, low variability between replicates gave very low MQL values. Where this was the case, a conservative approach was taken and a value equivalent to the concentration of the lowest calibration standard was used.

Estimated MQLs for BaP are given in Table 2-1. Offerman, et al., (4) have suggested that a monitoring method for PAHs should be sufficiently sensitive to detect BaP at an air

TABLE 2-2. REPORTED RECOVERIES OF SURROGATE PAHs FROM FIELD SAMPLES, CONTROLS AND BLANKS

	Spiked (ng)	% recovery[a] (n = ~417)
Fluorene-d_{10}	103	87 ± 26
Chrysene-d_{12}	19.9	89 ± 20
Benzo[e]pyrene-d_{12}	20.5	89 ± 23
Di-n-octylphthalate-d_4	101	88 ± 24

[a] Mean ± standard deviation.

concentration of 0.3 ng/m^3. This is the concentration for which it has been estimated that the risk of cancer for lifetime exposure is less than 1 x 10^{-6}. For this study, the median MQL for BaP was less than 0.1 ng/m^3 indicating that the method is sufficiently sensitive for exposure and health assessments.

Finally, analytical results for the field samples were evaluated to determine if interferences or other matrix effects prevented quantitation of the target PAHs and phthalates. With the exception of benzo[k]fluoranthene (BkF), interferences were not a problem. For BkF interferences from a large closely-eluting chromatographic peak prevented quantitation. Only at high BkF concentrations could BkF and the interfering peak be resolved and quantitation performed. In the remaining samples, BkF was reported as detected but was not quantitated.

2.2 DATA ANALYSIS

2.2.1 Objective 1: To Estimate Frequency Distributions for Residential Indoor Concentrations of PAHs and Phthalates in the Selected Study Area During a Single Season (Fall, 1990)

Objective 2: To Estimate Frequency Distributions for Residential Outdoor Concentrations of PAHs and Phthalates in the Selected Study Area During a Single Season (Fall, 1990)

The first step in data analysis was to determine the prevalence of target PAHs and phthalates in air samples. Table 2-3 provides data for the percentage of samples with air concentrations above the method quantifiable limits (percent quantifiable) in each of the four sample types (indoor/daytime, indoor/nighttime, outdoor/daytime, and outdoor/nighttime).

For the PAHs, percent quantifiable values ranged from a high of 100% for phenanthrene in indoor/daytime samples and benzo[ghi]perylene in outdoor/nighttime

TABLE 2-3. WEIGHTED PERCENT OF SAMPLES WITH REPORTED AIR CONCENTRATIONS ABOVE THE METHOD QUANTIFIABLE LIMIT

	Percent Quantifiable			
	Indoor		Outdoor	
Compound	Night	Day	Night	Day
<u>PAHs</u>				
<u>3-Rings</u>				
Acenaphthylene	76.3	77.9	86.8	67.5
Phenanthrene	98.9	100	90.1	92.7
Anthracene	87.6	86.4	73.2	69.5
<u>4-Rings</u>				
Fluoranthene	81.0	80.8	90.3	73.0
Pyrene	98.9	98.4	95.3	92.7
Benzo[a]anthracene	56.3	49.1	56.4	44.8
Chrysene	84.7	80.3	88.7	89.7
<u>5-Rings</u>				
Benzo[k]fluoranthene[a]	33.9	39.4	38.6	23.5
Benzo[e]pyrene	74.3	72.8	88.2	69.5
Benzo[a]pyrene	75.0	68.1	81.7	49.2
<u>6-Rings</u>				
Indeno[1,2,3-cd]pyrene	68.6	68.5	53.4	48.4
Benzo[ghi]perylene	87.7	89.4	100	79.9
<u>7-Rings</u>				
Coronene	77.4	77.5	84.6	60.1
<u>PHTHALATES</u>				
Diethylphthalate	98.4	94.9	17.0	14.2
Di-<u>n</u>-butylphthalate	99.0	100	61.5	52.6
Butylbenzylphthalate	95.7	93.8	11.0	11.9
Di-2-ethylhexylphthalate	99.0	100.0	25.8	61.0
Di-<u>n</u>-octylphthalate	30.5	36.1	1.8	1.8
Sample Size	113	115	53	42

[a] Unweighted estimate.

samples to a low of 44.8% for benzo[a]anthracene in outdoor/daytime samples. Benzo[k]fluoranthene was excluded from these analyses since reliable quantifiable limits could not be determined due to interferences in the samples. With the exception of benzo[a]anthracene, all of the 3- and 4-ringed PAHs had high percent quantifiable values (> 65%) and showed a similar pattern between sample types. On the other hand, most of the 5- to 7-ringed PAHs tended to show slightly lower percent measurable values. For these latter chemicals, outdoor/nighttime air samples gave the highest percent measurable values, whereas outdoor/daytime samples showed the lowest.

Except for di-n-octylphthalate, all of the phthalates were ubiquitous in indoor air samples with percent quantifiable values greater than 90%. Percent quantifiable values for phthalates in outdoor air samples were much lower ranging from a high value of 61.5% for di-n-butylphthalate in nighttime samples to a low value of 1.8% for di-n-octylphthalate in both daytime and nighttime samples. These data suggest that indoor phthalate concentrations arise from primarily indoor sources and that most of the exposure to airborne phthalates will occur indoors.

Concentration distributions using weighted analyses were then calculated for all of the PAHs and phthalates. Because of a problem with interferences during sample analyses, weighted statistics were not computed for benzo[k]fluoranthene. Air concentration data by sample type are given in Table 2-4. Results for benzo[a]pyrene are summarized graphically in Figure 2-1 which gives measured air concentrations in each of the four sample types.

Concentration data for the PAHs show several interesting trends. First, relative air concentrations for the individual PAH species in all four sample types show highest concentrations for the more volatile, 3- and 4-ringed species and lowest concentrations for the

TABLE 2-4. WEIGHTED AIR CONCENTRATIONS (ng/m^3) FOR PAHs AND PHTHALATES

	Indoor						Outdoor					
	Day		Night		Day-Night[a]		Day		Night		Day-Night	
Compound	Median	90th[b]	Median	90th	Median	90th	Median	90th	Median	90th	Median	90th
PAHs												
3-Rings												
Acenaphthylene	3.5	15	3.8	16	3.9	11	1.8	12	6.9	35	4.4	21
Phenanthrene	16	32	15	28	15	30	8.8	20	12	22	11	18
Anthracene	0.41	1.0	0.47	1.2	0.49	1.1	0.36	0.85	0.57	1.6	0.55	1.0
4-Rings												
Fluoranthene	1.7	3.1	1.6	2.8	1.6	2.8	2.2	4.8	2.3	4.1	2.2	4.5
Pyrene	1.8	3.6	1.6	2.7	1.8	2.8	1.8	4.1	2.0	4.0	2.0	3.9
Benzo[a]anthracene	NQ[c]	0.38	0.11	0.32	0.11	0.30	NQ	0.37	0.13	0.56	NQ	0.46
Chrysene	0.16	0.63	0.17	0.61	0.18	0.58	0.24	0.84	0.21	1.0	0.22	0.95
5-Rings												
Benzo[e]pyrene	0.17	0.60	0.15	0.47	0.15	0.51	0.13	0.59	0.22	0.85	0.18	0.60
Benzo[a]pyrene	0.14	0.77	0.20	0.70	0.19	0.65	0.09	0.35	0.19	1.4	0.16	0.84
6-Rings												
Indeno[1,2,3-cd]pyrene	0.42	1.7	0.39	1.4	0.39	1.4	NQ	1.2	0.34	1.6	0.30	1.2
Benzo[ghi]perylene	0.74	3.5	0.61	2.3	0.84	2.3	0.36	1.5	0.83	3.1	0.69	2.0
7-Rings												
Coronene	0.68	2.3	0.61	2.3	0.75	2.0	0.36	1.2	0.55	2.9	0.46	2.0
PHTHALATES												
Diethylphthalate	340	840	340	810	350	850	NQ	110	NQ	140	NQ	120
Di-n-butylphthalate	420	1300	390	1500	410	1500	16	33	18	57	18	47
Butylbenzylphthalate	34	140	35	120	35	140	NQ	5.3	NQ	6.7	NQ	NQ
Di-2-ethylhexylphthalate	110	240	93	170	103	215	28	65	NQ	38	NQ	45
Di-n-octylphthalate	NQ	9.7	NQ	4.6	NQ	6.7	NQ	NQ	NQ	NQ	NQ	NQ

[a] Concentration average for the combined 24-hour daytime and nighttime period.

[b] 90th percentile.

[c] Below the method quantifiable limit given in Table 2-1.

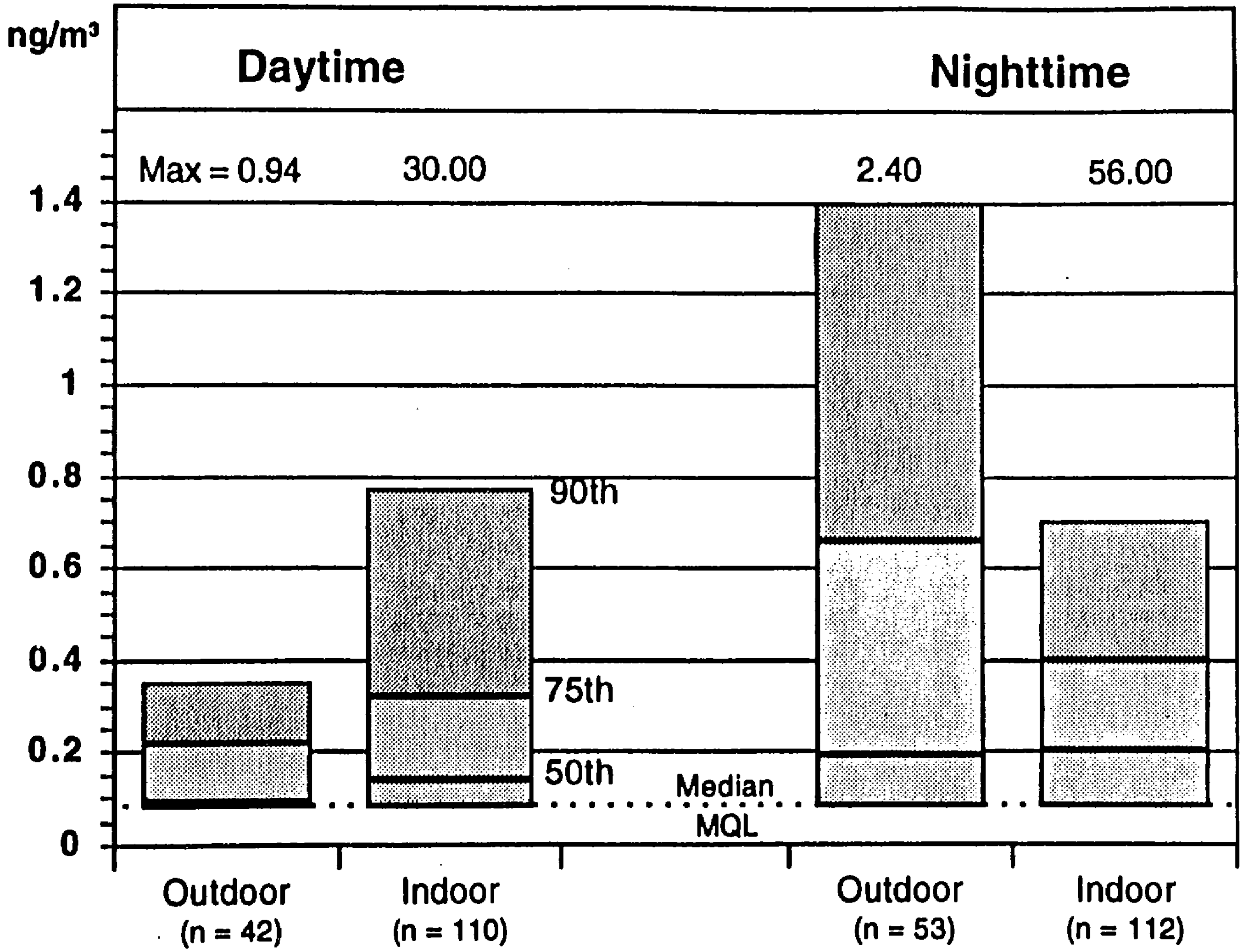


Figure 2-1. Weighted Distributions for Benzo[a]pyrene Concentrations in Indoor and Outdoor Air

particulate-phase 5-, 6-, and 7-ringed species. In evaluating these results, it should be kept in mind that the target PAHs are generated as a suite of chemicals during the combustion of organic materials such as wood, fossil fuels, and tobacco. Thus, theoretically when one PAH is found in a sample, all of the other target PAHs should also be present. In environmental samples, the volatile 3- and 4-ringed PAHs are usually at much higher concentrations than the less volatile 5- to 7-ringed species [4,5,18]. Highest median air concentrations were found for phenanthrene (8.8 to 16 ng/m^3) followed by acenaphthylene (1.8 to 6.9 ng/m^3), fluoranthene (1.6 to 2.3 ng/m^3), and pyrene (1.6 to 2.0 ng/m^3). Median concentrations for the particulate phase 5- to 7-ringed species were an order of magnitude lower with lowest median air concentrations reported for benzo[a]pyrene (0.09 to 0.20 ng/m^3) and benzo[e]pyrene (0.13 to 0.22 ng/m^3).

Second, indoor air samples showed little or no increase in median or mean air concentrations compared to outdoor concentrations. This is not an unexpected result since field monitoring was performed in the fall in southern California. The weather was generally moderate and based on the questionnaire responses there was little use of indoor heating appliances. This included woodstoves and fireplaces which are considered one of the primary sources of PAHs in indoor air. In addition, less than 30% of the homes reported any smoking.

The most striking trend in the concentration data is the considerably higher nighttime concentrations reported for outdoor samples compared to the daytime samples. For example, the median nighttime/outdoor air concentration for BaP was 0.19 ng/m^3 while the corresponding daytime concentration was less than half that value at 0.09 ng/m^3. This trend was seen for all of the particulate phase 5- to 7-ringed PAHs as well as the more volatile 3-ringed species.

Daytime/nighttime air concentration ratios for the weighted concentration statistics were calculated to further examine this trend. Results indicated that daytime/nighttime ratios were essentially close to one for indoor samples. Ratios for the geometric means ranged from 0.82 to 1.1, with only BaP (ratio 0.82) having a median daytime/nighttime concentration ratio less than 1.0. For outdoor samples, only the 4-ringed PAH fluoranthene showed geometric mean air concentration ratio greater than 0.90 with many compounds giving low daytime/nighttime concentration ratios. Acenaphthylene gave the lowest geometric means (0.39), arithmetic means (0.25) and the medians (0.20). These ratios indicate that the nighttime/outdoor concentration was approximately three times higher than the daytime/outdoor concentration for this compound. For BaP, ratios for the arithmetic means, geometric means and medians were 0.38, 0.48, and 0.50 respectively.

This outdoor daytime/nighttime concentration effect could have occurred for several reasons. Winds were higher during the daytime which could have dispersed and diluted PAH concentrations during the daytime. Alternately, photodegradation of PAHs may be occurring during the day (19,20). Under these conditions, PAHs that are generated at the same rate over a 24-hour period may react with sunlight during the day to effectively reduce daytime concentrations to give correspondingly low daytime/nighttime concentration ratios in outdoor samples.

Although most of the homes had low PAH concentrations in indoor air samples, two homes had substantially elevated levels. Indoor air concentration data from these two homes are given in Table 2-5. Indoor PAH air concentrations in the home with the next highest values were approximately an order of magnitude lower than the results reported for the two highest homes. These data are presented to show the "worst" case concentrations found in Riverside during field monitoring. Home 167 reported moderate smoking (~10 cigarettes)

TABLE 2-5. MEASURED INDOOR AIR CONCENTRATIONS (ng/m^3) IN THE TWO HOMES WITH THE HIGHEST LEVELS

	House 116		House 167	
Compound	Day	Night	Day	Night
PAHs				
3-Rings				
Acenaphthylene	530	2900	200	130
Phenanthrene	150	140	45	44
Anthracene	18	19	6.0	5.5
4-Rings				
Fluoranthene	40	34	11	13
Pyrene	92	79	22	23
Benzo[a]anthracene	2.3	2.3	0.90	0.86
Chrysene	2.9	3.0	1.2	1.4
5-Rings				
Benzo[k]fluoranthracene	26	35	6.7	5.8
Benzo[e]pyrene	15	19	3.7	2.9
Benzo[a]pyrene	30	56	7.9	4.9
6-Rings				
Indeno[1,2,3-cd]pyrene	49	64	7.5	7.0
Benzo[ghi]perylene	124	170	17	15
7-Rings				
Coronene	63	96	12	8.4
PHTHALATES				
Diethylphthalate	320	320	160	120
Di-n-butylphthalate	340	220	150	97
Butylbenzylphthalate	17	16	15	12
Di-2-ethylhexylphthalate	62	65	79	84
Di-n-octylphthalate	NQ[a]	NQ	NQ	4.9

[a] Below the method quantifiable limit.

during each of the two monitoring periods. No other obvious combustion activities or other sources were reported for either home that would serve as a major source for PAHs. Outdoor PAH air concentrations for these homes were also an order of magnitude lower than the measured indoor air concentrations. BaP concentrations were further analyzed as a final evaluation of the reported PAH air concentration data. BaP is a carcinogen and is currently under consideration by ARB as a toxic air contaminant. It has been estimated that an air concentration of 0.3 ng/m^3 over a 70-year exposure period will result in a 10^{-6} excess cancer risk (15). California's Office of Environmental Health Hazard Assessment has set a preliminary unit risk for BaP at 1.1×10^{-3} $(ng/m^3)^{-1}$. Using this preliminary number, it is estimated that an air concentration of ~0.9 ng/m^3 would give a 10^{-6} excess cancer risk (ARB, personal communication).

Table 2-6 shows the weighted percentage of air samples of each type that exceed the 0.3 ng/m^3 concentration. Percentages of samples that exceed 2 times (0.6 ng/m^3), 5 times (1.5 ng/m^3), and 10 times (3.0 ng/m^3) this level have also been given. Results show that a substantial fraction of the population may be exposed to BaP concentrations above the 0.3 ng/m^3 level. The home with the highest BaP levels had indoor air concentrations that are approximately two orders of magnitude higher than the (0.3 ng/m^3) risk level.

Evaluation of the air concentration data for the phthalates is straightforward. With the exception of di-n-octylphthalate, all of the phthalates showed high indoor air concentrations compared to the PAHs. Diethylphthalate and di-n-butylphthalate showed the highest indoor air concentrations with median daytime concentrations of 340 and 420 ng/m^3, respectively. Median outdoor air levels for the phthalates were at least an order of magnitude lower than the corresponding indoor levels. Di-n-octylphthalate had median concentrations below the quantifiable limit (ng/m^3) for all four sample types.

TABLE 2-6. WEIGHTED PERCENTAGE OF AIR SAMPLES WITH BaP CONCENTRATION EXCEEDING SELECTED LEVELS

	Percentage			
Sample Type	≥ 0.3 ng/m^3	≥ 0.6 ng/m^3	≥ 1.5 ng/m^3	≥ 30 ng/m^3
Indoor-day	25.2	12.4	2.0	1.3
Indoor-night	39.7	12.0	2.0	1.3
Outdoor-day	15.8	3.9	0	0
Outdoor-night	37.6	25.2	7.6	0

2.2.2 Objective 3: To Evaluate Whether PAH and Phthalate Exposures are Principally from Indoor or Outdoor Microenvironments in the Selected Study Area During a Single Season (Fall, 1990)

Objective 4: To Estimate the Contribution of Outdoor Levels of PAHs and Phthalates to Indoor Levels in the Selected Study Area During a Single Season (Fall, 1990)

As a first step in studying the relationship of the target PAHs and phthalates between indoor and outdoor samples, indoor/outdoor air concentration ratios were calculated and summary statistics generated for these ratios. Unweighted data on indoor/outdoor air concentration ratios are provided in Table 2-7. Ratios were calculated only if both concentrations were quantifiable. Results are given for both daytime and nighttime samples.

For the PAHs, the highest geometric mean ratios for indoor/outdoor air concentrations were calculated for acenaphthene (2.6), phenanthrene (2.0), and benzo[a]pyrene (1.8) in daytime samples. The highest median indoor/outdoor air concentration ratios were calculated for phenanthrene (1.9) and benzo[a]anthracene (1.9) in daytime samples. As with the concentration data, a daytime/nighttime trend is seen for these calculated indoor/outdoor concentration ratios. For daytime samples, all the target PAHs except fluoranthene had median and geometric mean indoor/outdoor air concentration ratios greater than one indicating higher indoor air concentrations during the day. For the nighttime samples, except for phenanthrene both geometric mean and median indoor/outdoor air concentration ratios were less than one indicating higher outdoor concentrations. If we consider that indoor air concentrations were essentially constant between the daytime and nighttime monitoring periods, then these results reflect the substantially lower daytime air concentrations measured in outdoor samples. Very high indoor/outdoor air concentration ratios were found in some homes indicating that high

TABLE 2-7. UNWEIGHTED SUMMARY STATISTICS FOR THE INDOOR/OUTDOOR AIR CONCENTRATION RATIO - QUANTIFIABLE AMOUNT ONLY[a]

	Indoor/Outdoor Concentration Ratio					
	Nighttime			Daytime		
Compound	n	Geometric Mean	Median	n	Geometric Mean	Median
PAHs						
3-Rings						
Acenaphthylene	28	0.62	0.45	22	2.6*	1.5
Phenanthrene	42	1.2*[b]	1.3	37	2.0*	1.9
Anthracene	32	0.91	0.66	22	1.4	1.1
4-Rings						
Fluoranthene	34	0.82	0.75	30	0.88	0.76
Pyrene	44	0.85	0.79	37	1.2	1.1
Benzo[a]anthracene	17	0.85	0.65	9	1.7	1.9
Chrysene	36	0.71*	0.66	23	0.79	0.72
5-Rings						
Benzo[e]pyrene	32	0.77	0.67	21	1.3	1.1
Benzo[a]pyrene	32	0.87	0.64	15	1.8	1.2
6-Rings						
Indeno[1,2,3-cd]pyrene	25	0.93	0.83	13	1.6	1.2
Benzo([ghi]perylene	40	0.82	0.68	29	1.4	1.3
7-Rings						
Coronene	31	0.89	0.85	23	1.4	1.4
PHTHALATES						
Diethylphthalate	8	2.3	3.2	6	3.0*	4.3
Di-n-butylphthalate	27	15*	15	19	16*	14
Butylbenzylphthalate	5	5.5*	8.9	5	4.6*	4.3
Di-2-ethylhexylphthalate	12	2.8*	3.1	19	2.2*	1.7
Di-n-octylphthalate	1	0.85	0.85	1	1.4	1.4

[a] In both indoor and outdoor samples

[b] Asterisk indicates that value is significantly different from one at the 0.05 level

indoor air concentrations may be present, whereas the range of outdoor air concentration range is narrower.

The phthalates showed indoor/outdoor concentration ratios greater than one suggesting relatively strong indoor sources. Highest ratios were calculated for di-n-butyl-phthalate (14-16). No conclusions can be drawn about di-n-octyl-phthalate because it was quantified in so few samples.

To further investigate the indoor/outdoor relationship, Spearman's rank correlations between indoor and outdoor air concentrations measured for samples collected at the same home during the same time period were computed. Data are provided separately for daytime and nighttime samples in Table 2-8. The table also shows which correlations are significant (i.e., judged to be greater than zero) at the 0.05 level. There appears to be little difference in the indoor/outdoor correlations for either the daytime or nighttime monitoring period. Highest correlations are seen for the 5-, 6-, and 7-ringed particulate-bound PAHs.

These indoor/outdoor correlations for PAHs are generally higher than those reported previously for volatile organic compounds (21,22). They are also considerably higher than the correlations computed for the phthalates. The strong correlations for PAHs suggest that outdoor PAHs may have made a substantial contribution to measured indoor concentrations. On the other hand, the high indoor/outdoor concentration ratios for the phthalates and the low indoor/outdoor correlations suggest again that the target phthalates are coming primarily from indoor sources and that outdoor sources do not provide a substantial contribution to indoor phthalate concentrations.

Finally, indoor source strengths were calculated for the PAHs and phthalates using a simple indoor air model. Source strengths were computed using all homes where measurements were performed. When a target chemical was not detected in a sample, a

TABLE 2-8. SPEARMAN'S RANK CORRELATION BETWEEN INDOOR AND OUTDOOR AIR SAMPLES[a]

Compound	Daytime Samples	Nighttime Samples
<u>PAHs</u>		
<u>3-Rings</u>		
Acenaphthylene	0.58[b]	0.51[b]
Phenanthrene	0.54[b]	0.60[b]
Anthracene	0.30	0.37
<u>4-Rings</u>		
Fluoranthene	0.55[b]	0.59[b]
Pyrene	0.52	0.44
Benzo[a]anthracene	0.51	0.52[b]
Chrysene	0.62[b]	0.59[b]
<u>5-Rings</u>		
Benzo[e]pyrene	0.71[b]	0.66[b]
Benzo[a]pyrene	0.72[b]	0.69[b]
<u>6-Rings</u>		
Indeno(1,2,3-cd)pyrene	0.69[b]	0.79[b]
Benzo(ghi)perylene	0.82[b]	0.78[b]
<u>7-Rings</u>		
Coronene	0.80[b]	0.76[b]
<u>PHTHALATES</u>		
Diethylphthalate	0.55	0.52[b]
Di-<u>n</u>-butylphthalate	0.20	0.11
Butylbenzylphthalate	0.16	0.16
Di-2-ethylhexylphthalate	0.16	0.28
Di-<u>n</u>-octylphthalate	0.28	0.31

[a] Computed using all samples.

[b] Significantly different from zero at the 0.05 level.

concentration equal to one-eighth of the MQL was used. Average 24-hour source strength terms were used to minimize the effects caused by differences in measured daytime and nighttime air concentrations measured outdoors. Source strength values calculated for the median and 75th percentile are summarized in Table 2-9. Results show low calculated source strengths for the PAHs. Phenanthrene gave the highest median value (2.0 µg/h). The median calculated source strength for benzo[a]pyrene was 0.01 µg/h. In contrast, the phthalates showed much higher calculated source strengths with median values of 55 and 92 µg/h for diethylphthalate and di-n-butylphthalate respectively. These results again suggest strong indoor sources for the phthalates.

Using a simple indoor air quality model and assuming steady-state conditions, the contribution of outdoor pollutant levels to indoor concentration (C_{oi}) is equal to

$$C_{oi} = \textit{Outdoor Concentration} \times \textit{Penetration Factor}$$

The fractional contribution of outdoor levels to indoor air concentrations (F_{oi}) may then be calculated as

$$F_{oi} = \frac{C_{oi}}{\textit{Indoor Concentration}}$$

Using this equation, high F_{oi} values mean that a high fraction of indoor pollutant levels are coming from outdoor sources. As with source strengths, 24-hour time weighted averages were used. Median F_{oi} values for PAHs ranged from 0.31 to 0.97. Highest median F_{oi} values were calculated for acenaphthylene (0.97) lowest for phenanthrene (0.31). The median F_{oi} value for BaP was calculated as 0.55. In contrast, for the phthalates, only a small fraction of indoor air levels come from outdoor sources. The highest median F_{oi} value was calculated for di-2-ethylhexyl-phthalate (0.25), whereas the lowest value was calculated for di-n-butyl-phthalate (0.07).

TABLE 2-9. 24-HOUR TIME WEIGHTED AVERAGE SOURCE STRENGTH (µg/h) VALUES[a]

Compound	N[b]	Source Strength (µg/h) Median	Source Strength (µg/h) 75th Percentile
PAHS			
3-Rings			
Acenaphthylene	27	0.00	0.07
Phenanthrene	30	2.0	0.36
Anthracene	28	0.04	0.09
4-Rings			
Fluoranthene	30	0.07	0.24
Pyrene	30	0.16	0.37
Benzo[a]anthracene	26	0.00	0.02
Chrysene	24	0.00	0.03
5-Rings			
Benzo[e]pyrene	29	0.00	0.02
Benzo[a]pyrene	28	0.01	0.03
6-Rings			
Indeno[1,2,3-cd]pyrene	25	0.00	0.10
Benzo[ghi]perylene	27	0.03	0.09
7-Rings			
Coronene	30	0.02	0.11
PHTHALATES			
Diethylphthalate	30	55	130
Di-n-butylphthalate	30	92	180
Butylbenzylphthalate	30	7.0	20
Di-2-ethylhexylphthalate	30	17	24
Di-n-octylphthalate	29	0.24	0.65

[a] Calculated assuming a penetration factor of 0.5.
[b] Number of homes.

It should be stressed that due to the many assumptions that must be made and the uncertainty associated with the use of a simple indoor air model, the analysis performed here on source strength and the fractional contribution was not intended to be a rigorous treatment of the data. Rather, it was intended to be a preliminary assessment that might be used to evaluate trends in the measured air concentration data.

2.2.3 Objective 5: Correlate PAH and Phthalate Concentrations with Other Pollutant Data Collected on PTEAM

Correlations between compounds in indoor and outdoor air samples were computed to evaluate the degree of association between these compounds. Spearman's rank correlations using all samples, were computed for the PAHs and phthalates measured as part of this chemical characterization study and for respirable particulate (PM_{10}), inhalable particulate ($PM_{2.5}$), and selected elements (lead and manganese) measured as part of the PTEAM study.

Spearman's rank correlations among PAHs in outdoor air samples were high and generally significantly greater than zero at the 0.05 level in both daytime and nighttime samples. Highest correlations (> 0.85) occurred among the particulate-phase 5- to 7-ringed PAHs. Most of the other compounds showed correlations greater than 0.60. The 3-ringed PAHs, most notably phenanthrene, gave the poorest correlations with the particulate-phase species, although these 3-ringed species correlated fairly well with each other and the 4-ringed congeners.

High correlations may suggest a common source for different chemicals. This is expected to be the case for the PAHs which are generated principally as combustion products of organic material such as woods, fossil fuels, and tobacco.

Comparison of correlations computed for daytime and nighttime samples showed little difference between samples collected during the two monitoring periods. Generally, where there was a difference, nighttime samples exhibited higher correlations. Again, phenanthrene was an exception, with higher correlations for daytime samples.

Spearman's rank correlations among PAHs computed for indoor air samples were also high among most compounds although comparisons of these results with those generated for outdoor air samples show several interesting trends. As with the outdoor samples, the particulate phase 5- to 7-ringed PAHs showed strong correlations (0.72 to 0.95) with each other. In contrast, the vapor-phase 3- and 4-ringed species showed much poorer correlations (generally less than 0.40) compared to the outdoor samples. Poorest correlations were computed for phenanthrene (less than 0.30) with particle-phase PAHs.

If outdoor sources provide the primary contribution to indoor PAHs, then different penetration rates from outdoors to indoors could result in poorer correlations. Alternatively, the indoor decay rate could be different for different PAHs and thus affect their degree of association.

Correlations among most phthalates, especially in indoor air samples, were poor (< 0.5). Highest correlations indoors occurred between diethylphthalate and di-n-butylphthalate (0.43) and between di-n-octylphthate and di-2-ethylhexylphthalate (0.61). The calculated Spearman's rank correlations were not substantially different for daytime and nighttime samples, either indoors or outdoors. Correlations between phthalates in outdoor air samples were higher than those found indoors. Butylbenzylphthalate was highly correlated (~0.60) with all the phthalates outdoors except diethylphthalate. Again, fairly strong correlations (0.68) were seen between di-n-octylphthalate and di-2-ethylhexylphthalate in outdoor air samples. Results for the outdoor samples should be viewed with some caution, since only very low levels of the phthalates were measured in outdoor samples. Under these conditions, high correlations could be a result of an experimental artifact such as background contamination generated during sample processing.

Spearman's rank correlations among the phthalates, PAHs, and PTEAM pollutants were also computed. For correlations among the phthalates and PAHs, only phenanthrene and diethylphthalate gave correlations greater than 0.50. Good correlations were found between these compounds in daytime/indoor (0.62), daytime/outdoor (0.60), and nighttime/outdoor (0.52) samples. In contrast, the correlation for daytime/outdoor (0.19) samples was low. Correlations between the phthalates and PTEAM pollutants were less than 0.50 in all four sample types. The only exception to this was the 0.62 correlation coefficient computed between butylbenzylphthalate and lead (10 µm fraction) in outdoor/nighttime samples, although the reason for this is unknown.

Spearman's rank correlations among PAHs and the PTEAM pollutants computed for outdoor samples show several trends:

(1) Correlations between lead and manganese and the PAHs were generally high (> 0.50),

(2) Highest correlations between the elements and PAHs were seen for the less volatile PAHs in nighttime samples and with the 10 µm fraction of the elemental samples.

(3) Few strong correlations were observed between the PAHs and particulates. Only phenanthrene and particulates in nighttime samples gave correlation coefficients greater than 0.60.

(4) Correlations between PAHs and particulates were generally higher in nighttime samples. Correlations of PAHs and PM_{10} and $PM_{2.5}$ were generally similar.

The same general trends were seen for the correlation among pollutants computed for indoor samples. Correlations between the PAHs and particulates were slightly higher for indoor samples, whereas correlations between PAHs and manganese were slightly lower for indoor air samples.

2.2.4 Objective 6: To Investigate the Possible Sources and Activities Contributing to Residential Indoor Levels of PAHs and Phthalates in the Selected Study Area During a Single Season (Fall, 1990)

Objective 7: To Examine the Contribution of Environmental Tobacco Smoke (ETS) to Indoor Levels of PAHs and Phthalates for the Selected Study Area During that Season

Selected questions from the study questionnaire were analyzed to determine if certain activities were related to elevated levels of PAHs and phthalates in air samples. Table 2-10 lists the questions that were asked to evaluate specific sources of the target PAHs and phthalates. The number of homes that fell into each category is also given. For each potential source category, arithmetic mean air concentrations and their standard errors were determined for the two groups identified from questionnaire responses (i.e., homes with and without potential sources).

Pairwise t-tests were performed to test for group differences using the arithmetic mean air concentrations. Since there were very few homes in each source group and since only a small fraction of indoor PAH concentrations appear to be from indoor sources, this analysis should only be expected to show a difference in mean air concentrations between source and non-source groups when a very strong source is present. Data from the two homes with the very high indoor air concentrations were not used during this analysis since it was felt these data would overwhelm any other effects.

TABLE 2-10. QUESTIONS AND REPORTED FREQUENCIES FOR POTENTIAL POLLUTANT SOURCES

		Number of Homes[a]			
		Day		Night	
Category	Question	Yes	No	Yes	No
Busy Road	Is the house located within 100 yards of a busy roadway?	42	55	39	56
Cooking	Did you do any indoor cooking, grilling or frying while you were at home? Was any cooking, grilling, or frying done in your home by someone else?	46	69	28	85
Smoking	Were any cigarettes, pipefuls of tobacco, and/or cigars smoked in your house during this period?	18	94	22	90
Other Smoke	Were there any other sources of smoke present in the home during this period such as burnt food or candles?	6	107	10	102
Car Start	Was a vehicle started or run in a garage attached to your home during this period?	18	83	5	99
Other[b]	Was natural ventilation open doors or windows used in your home during the period?	96	27	79	45
	Was central air conditioning or heating used in your home during this period?	23	101	19	105
	Was a whole house or attic fan used in your home during this period?	2	122	3	121
	Was an ultrasonic or cool mist humidifier used in your home during this period?	4	120	1	122
	Was a filtration system (including filters, ionizers, and electrostatic precipitators) used in your home during this period?	0	124	0	124
	Was an unvented kerosene heater used in your home during this period?	0	124	0	124
	Was a fireplace used in your home during this period?	1	123	1	123
	Was a wood-burning stove used in your home during this period?	0	124	0	124

[a] Number of homes in each category that had valid data for air concentration measurements and questionnaire response.
[b] Number of homes in each category that had questionnaire response.

Results for smoking show elevated indoor air concentrations for the PAHs in both daytime and nighttime samples. Only phenanthrene and anthracene in nighttime samples are exceptions to this trend. The greatest relative differences in mean air concentrations were seen for chrysene and the particulate phase 5-, 6-, and 7-ring PAH species. For these chemicals, indoor concentrations measured in homes with smoking were approximately 1.5 to 2.0 times higher than in homes without smoking. Indoor air concentrations were significantly higher (0.05 level) in homes where smoking occurred compared to homes without smoking for acenaphthylene, fluoranthene, benzo[a]anthracene, chrysene, benzo[e]pyrene, benzo[a]pyrene, and indeno[1,2,3-cd]pyrene in both daytime and nighttime samples. Significantly higher air concentrations (0.05 level) were also found for benzo[ghi]perylene and coronene in daytime samples. Homes where smoking took place also showed elevated indoor concentrations for diethylphthalate, butylbenzylphthalate, and di-2-ethylhexylphthalate although the difference was not statistically significant at the 0.05 level. Homes with cooking and other smoke sources exhibited slightly higher (but not significant at the 0.05 level) air concentrations of some of the PAHs and phthalates.

Participants who reported that an automobile was started in an attached garage on the day of monitoring showed higher di-n-butylphthalate air concentrations in both daytime and nighttime indoor air samples. No differences in indoor air concentrations were evident for any of the PAHs due to attached garage use.

The effect of proximity on a busy roadway to both indoor and outdoor air concentrations at a home was also examined. Outdoor/nighttime samples showed the greatest difference in PAH concentrations when comparing homes that were situated near a busy roadway to homes that were not. Both daytime and nighttime samples showed a small elevation in indoor air concentrations for the particulate phase PAHs, although the differences between the two categories of homes were not significant at the 0.05 level.

To further evaluate the effect of smoking, indoor/outdoor air concentration ratios were calculated for each home where quantifiable values were found in both samples. Mean concentration ratios were then calculated for homes with and without smoking. Results show only small increases in PAH indoor/outdoor concentration ratios in homes where smoking took place. Unfortunately, there were only a very small number of homes in the smoking group and no further analyses were performed with the data.

SECTION 3

RECOMMENDATIONS

This study has provided important data that can be used by ARB in its exposure and risk assessment process by providing residential indoor air and outdoor air concentration data for selected PAHs and phthalates in Riverside, California. Additional work is recommended that would broaden the scope of the database generated during this study. Recommendations are listed in order of overall priority.

- Methods that were used here should be applicable to personal exposure monitoring. Previous studies for volatile organic compounds and particulates showed elevated air concentrations for personal exposure samples compared to either indoor or outdoor air samples (21,22). A study that incorporates personal exposure monitoring for the PAHs and phthalates should be performed. Results could then be used to assess actual exposure levels as well as establish the relationship between personal exposure and indoor and outdoor air concentrations. Data could also be used to evaluate the approach that should be taken to model exposure based on measured microenvironmental concentrations.
- More detailed information should be obtained to evaluate sources and activities that affect PAH and phthalate exposure. The effect of specific combustion sources on air concentrations for PAHs should be evaluated. In addition, the reason for the very high PAH concentrations in two of the homes of this study should be investigated by performing additional monitoring in these homes. During the same visit, the homes should be evaluated thoroughly for potential sources of PAHs. Potential indoor sources for

phthalate contamination should also be explored through emissions testing of common household materials and consumer products.

- Studies should be performed to better define the parameters used to model indoor source strengths and pollutant concentrations. The indoor and outdoor pollutant decay rates and the penetration rates for pollutants into buildings need to be better understood.
- Additional monitoring should be performed in Riverside during a winter season. Previous studies for VOCs have shown substantially higher pollutant concentrations in Los Angeles during the winter (22). This trend may be greater for PAHs which are generated as a result of various heating sources. If PAH concentrations are significantly higher in the winter, it is essential that these data are generated and used for the required exposure and risk assessments.
- Finally, specific chemical markers (i.e., nicotine or quinoline) that identify specific combustion sources (i.e., cigarette smoking) should be developed and applied in future field studies.

SECTION 4

PTEAM OVERVIEW

This project for the chemical characterization of PAHs and phthalates in air samples was performed as part of the PTEAM main study. This collaborative research effort provided several important advantages to the ARB:

- Significant cost savings were possible since EPA funded the survey design and survey operation aspects of the overall study.
- Data collected for the PTEAM main study on household characteristics and chemical source use were available to this project for statistical analysis.
- Finally, a joint effort with EPA necessitated that a site in California be selected for the PTEAM main study; all information generated on the PTEAM main study are therefore available for assessing particulate exposures in California.

As an overview, the procedures used on the PTEAM main study and conclusions relating to major study elements are summarized below. The implementation and results of the program are described in detail in a separate report (23).

4.1 PTEAM PROGRAM OBJECTIVES

The primary objective of the PTEAM program was to estimate the frequency distribution of exposure of an urban population to inhalable (PM_{10}) and respirable ($PM_{2.5}$) particles that could be used to make health risk assessments.

Several specific aims were identified as important elements of the primary objective including:

- To provide the probability-based monitoring information for determining the frequency distribution of exposure.
- To measure human exposure to inhalable and respirable particles for health risk assessments.
- To define the relationship between personal exposure, microenvironmental/ambient air levels, and outdoor ambient air standards.
- To determine the sources of particles.
- To develop a source apportionment or source receptor model for exposure to particles using source profile and mass measurement data.

Personal exposure monitoring was used to measure actual exposure to target pollutants, whereas the fixed indoor and outdoor monitoring at each home were used to determine the relative contribution of indoor and outdoor sources to personal exposure. Ambient monitoring at a central site was used to provide a macroenvironmental measurement of exposure for the pollutants. Questionnaires were used to obtain information on exposure to particulates during monitoring. PM_{10} data were used to investigate relationships between indoor exposure and ambient air standards.

The combination of mass and chemical measurements provided the information for determining the frequency distribution of exposure. Mass concentration measurements were made gravimetrically to provide an index of particle exposure. Filter samples used for mass measurement were analyzed for elements. Results of the elemental analysis were used to estimate exposure and as inputs to source receptor modeling. Nicotine was measured as a tracer of environmental tobacco smoke (ETS), and was to be used to assess the contribution of ETS to personal exposure of inhalable and respirable particles.

4.2 SURVEY DESIGN AND OPERATIONS

Riverside, California was selected as the site for the PTEAM study because it is an urban area that was known to have high variability of outdoor inhalable particulate concentrations and because the socioeconomic characteristics of the community appeared to provide a microcosm of the Southern California population. In addition, outdoor particle levels are not dominated by a single stationary source. Probability sampling methods were used to select the study participants since they provide the only widely accepted basis for making inferences from a sample to the target population. Population units sampled for data collection were person-days because the observed sampling outcome depended upon the time during which the measurements were performed. The sample was designed to give data for 175 participants representing 139,000 non-smoking residents age 10 and above. People working at least 30 hours per week outside their home and people exposed to passive smoking within their homes were slightly oversampled to support separate statistical analyses. Similarly, the indoor/outdoor microenvironmental monitoring was designed to represent 61,520 households containing at least one non-smoker age 10 or older in the targeted area of Riverside.

Efforts were made to improve participant response through press coverage and a mailing of an information packet that contained a brochure with the EPA and ARB logo and a cover letter signed by several officials, including the mayor. Potential participants remembered the press coverage and the interviewers had more credibility when approaching participants during household screening interviews. Screening interviews, participant selection, and participant recruitment were conducted during one interviewer visit. One hundred and seventy-eight persons were successfully recruited into the study to give an overall response rate of 49%. This is similar to response rates achieved on many previous personal monitoring studies that required several visits to the participant's home and the burden of wearing a chemical monitor for 24 hours. Questionnaires were designed to obtain information about the participant's locations, activities, and potential exposure to particle sources during each 12-hour monitoring period. These questionnaires were successfully administered to all study participants.

4.3 FIELD MONITORING AND METHODS

The PTEAM field monitoring main study was designed to collect sufficient samples to characterize the exposure of a representative population in Riverside, California to inhalable particulates. A total of 178 persons were selected for monitoring; each was monitored for two consecutive 12-hour periods. During each monitoring period, several air samples were scheduled for collection, including one personal PM_{10}, one indoor PM_{10}, one indoor $PM_{2.5}$, one outdoor PM_{10}, and one outdoor $PM_{2.5}$ sample. Approximately four persons were monitored each day from September 22 through November 9, 1990. Additional samples were collected to measure nicotine air concentrations and air exchange rates in each study home to provide source characterization data. A monitoring site was set-up at one location in Riverside to monitor ambient concentrations of particulates during each 12-hour period throughout the course of the study. Reference method PM_{10} and dichotomous samplers were operated at this temporal site alongside personal and stationary monitors identical to those used for participant monitoring. A mobile laboratory was set-up in Riverside for performing all particulate filter weighing operations. An overview of sample collection and analysis methods is given in Table 4-1. An overview of the total number of samples collected and analyzed is given in Table 4-2.

TABLE 4-1. SAMPLING AND ANALYSIS METHODS USED DURING PTEAM

Sample Type	Collection	Analysis
Personal Exposure Monitor (PEM-10 µm)	Portable battery operated cassette pump pulled air through a portable impactor worn by participant. Impactor contained 37-mm Teflon filter with a 2 µm pore size. Flow rate 4 L/min over 12 hours.	Gravimetric for particle mass. XRF for elemental concentration.
Stationary Indoor Monitor (SIM)/Stationary Ambient Monitoring (SAM) (2.5 and 10 µm)	Electronically flow-controlled Medo pump pulled air through a stationary impctor. Impactors with particle size cuts of 10 µm and 2.5 µm wre used with 37-mm Teflon filters having a 2-µm pore size. Flow rate 4 L/min over 12 hours.	Gravimetric for particle mass. XRF for elemental concentration.
Dichots	Sierra dichotomous sampler consisted of a sampling head connected to an air sampling pump. A 10 µm aerodynamic diameter and a 2.5 µm aerodynamic diameter fraction are collected on two Teflon filters.	Gravimetric for particle mass. XRF for elemental concentrations.
SSI (PM_{10})	Wedding sampler consisting of a large air sampling pump and sampling head that trapped particles up to 10 µm onto a 8 x 10" glass fiber filter with a 2-µm pore size at a constant flow of 1.13 m^3/min for 12 hours.	Gravimetric for particle mass.
Cascade	Anderson cascade impactor consisting of an air sampling pump plus eight stages for particle collection by size. Impaction media were 3" ID glass fiber filters with a 2-µm pore size. Flow rate of 28 L/min for 3.5 to 10 day periods.	Gravimetric for particle mass.
Air Exchange	Perfluorotracer (PFT) released into home at a known rate, then collected on sorbent capillary diffusion tube.	Thermal desorption of tube for gas chromatography with electron capture detection to determine PFT concentration. Air exchange rate calculated from PFT concentrations, collection rate, release rate, and house volume.
Nicotine	All PEM, SIM and SAM sampling heads contained a citric acid impregnated glass fiber backing filter to trap nicotine out of the air stream being sampled. A portion of these samples were analyzed.	Filter solvent desorbed; extract analyzed by gas chromatography

TABLE 4-2. SAMPLE COLLECTION STATUS FOR PTEAM 1990 STUDY

		Scheduled (Work Plan)/Attempted/Collected			
Sample type	Location	Samples	Duplicates	Blanks	Total
PEM (10 µm)	Participant	350/356/347	0/0/0	18/17/17	368/373/364
	Technician	20/17/16	20/17/17	0/0/0	40/34/33
	Temporal Site	88/96/88	4/3/3	0/1/1	92/100/92
SIM/SAM (2.5 µm)	Indoor	350/356/341	18/17/15	18/17/16	386/390/372
	Outdoor	350/350/334	18/17/17	0/0/0	368/367/351
	Temporal Site	88/96/92	4/3/3	0/1/1	92/100/96
SIM/SAM (10 µm)	Indoor	350/355/333	18/17/17	18/17/16	386/389/366
	Outdoor	350/350/336	18/17/17	0/0/0	368/367/352
	Temporal Site	88/96/91	4/4/4	0/1/1	92/101/96
Air Exchange	Indoor	1050/1060/1046	50/356/350	40/94/87	1140/1510/1483
Nicotine	Participant	350/356/347	0/0/0	18/18/16	368/374/363
	Indoor	350/355/336	18/17/16	18/17/16	386/389/366
	Technician	20/17/16	20/17/17	0/0/0	40/34/33
Dichots					
Fine	Temporal Site	88/96/95	88/96/95	0/21/19	176/213/209
Coarse	Temporal Site	88/96/95	88/96/94	0/21/18	176/213/207
SSI (PM_{10})	Temporal Site	88/96/92	88/96/88	0/44/43	176/236/223
Cascade[a]	Temporal Site	30/40/32	15/0/0	4/0/0	49/40/32

[a] Five cascade runs attempted, four successful, 8 filter stages each.

Over 95% of the personal and stationary particulate samples, nicotine samples, and air exchange samples were successfully collected as scheduled. All filters were weighed on-site in the laboratory under controlled conditions of temperature and humidity. All sample collection and weight data were entered directly into computers in the field to reduce data transcription errors and facilitate construction of the database. The only significant portion of data not collected as intended during the study was measurement of meteorological conditions at the temporal site. Meteorological data were obtained from three airports in the vicinity of Riverside to supplement the data from the temporal site.

The particle sample collection and weighing methods performed very well. Sample collection and weighing precision was better than 5% relative standard deviation for most collocated particle samplers. The median particle filter background was 9 μg as measured on field blank filters. Over 85% of the filters that were re-weighed for quality control purposes passed the maximum ± 4 μg tolerance on the first pass. All of the filters passed the tolerance criteria before the weight data were accepted. Procedures were implemented that streamlined filter handling and reduced filter contamination.

Data were incomplete for nicotine analysis. As a consequence, results for nicotine concentrations in air samples collected as part of the PTEAM study have not been reported here.

4.4 PARTICLE AND ELEMENTAL CONCENTRATION DATA

4.4.1 Particle Concentration Distributions

A primary goal of this research was to measure the distribution of exposure of an urban population and compare it to the 150 $\mu g/m^3$ PM_{10} National Ambient Air Quality Standard (NAAQS) and the 50 $\mu g/m^3$ California Ambient Air Quality Standard (CAAQS). Total 24-hour personal exposure concentrations, measured as person-days, were calculated as a time-weighted average across two consecutive measurement periods of approximately 12 hours each. Personal exposure monitors (PEM) were used to measure particle concentrations in the participant's breathing zone while stationary indoor (SIM) and stationary ambient monitors (SAM) were used to measure particle concentrations inside and outside the home. Approximately 25% of the person-days exceeded the 150 $\mu g/m^3$ level and over 90% of the person-days exceeded the 50 $\mu g/m^3$ level during this study (Figure 4-1). The median 24-hour concentration for personal exposure to PM_{10} was 102 $\mu g/m^3$ with a range from 34 to 287 $\mu g/m^3$. Personal exposure concentrations were greater than those measured both inside and outside of residences using SIM and SAM microenvironmental monitors. They were also higher than concentrations measured at the ambient air monitoring site using several different methods. These data indicate that a substantial portion of the population was exposed to particle levels higher than the NAAQS and most of the population's exposure exceeded the CAAQS. Outdoor air concentrations of PM_{10} at the residences were greater than 150 $\mu g/m^3$ on approximately 15% of the household-days. Indoor and outdoor 24-hour PM_{10} levels were above 50 $\mu g/m^3$ during over 70% of the household-days during this study.

Particle concentration levels were also examined on a daytime/nighttime basis. Daytime personal exposure PM_{10} concentrations were much higher, as a whole, than daytime indoor or outdoor PM_{10} levels. Daytime personal exposure concentrations ranged from 35 to 455 $\mu g/m^3$ with a median concentration of 130 $\mu g/m^3$. In contrast, nighttime personal exposure concentrations were lower than those measured outdoors and only slightly higher than indoor levels of PM_{10}. Nighttime personal exposure concentrations ranged from 19 to 278 $\mu g/m^3$ with a median concentration of 66 $\mu g/m^3$. Daytime indoor PM_{10} concentrations ranged from 17 to 513 $\mu g/m^3$ with a median concentration of 82 $\mu g/m^3$.

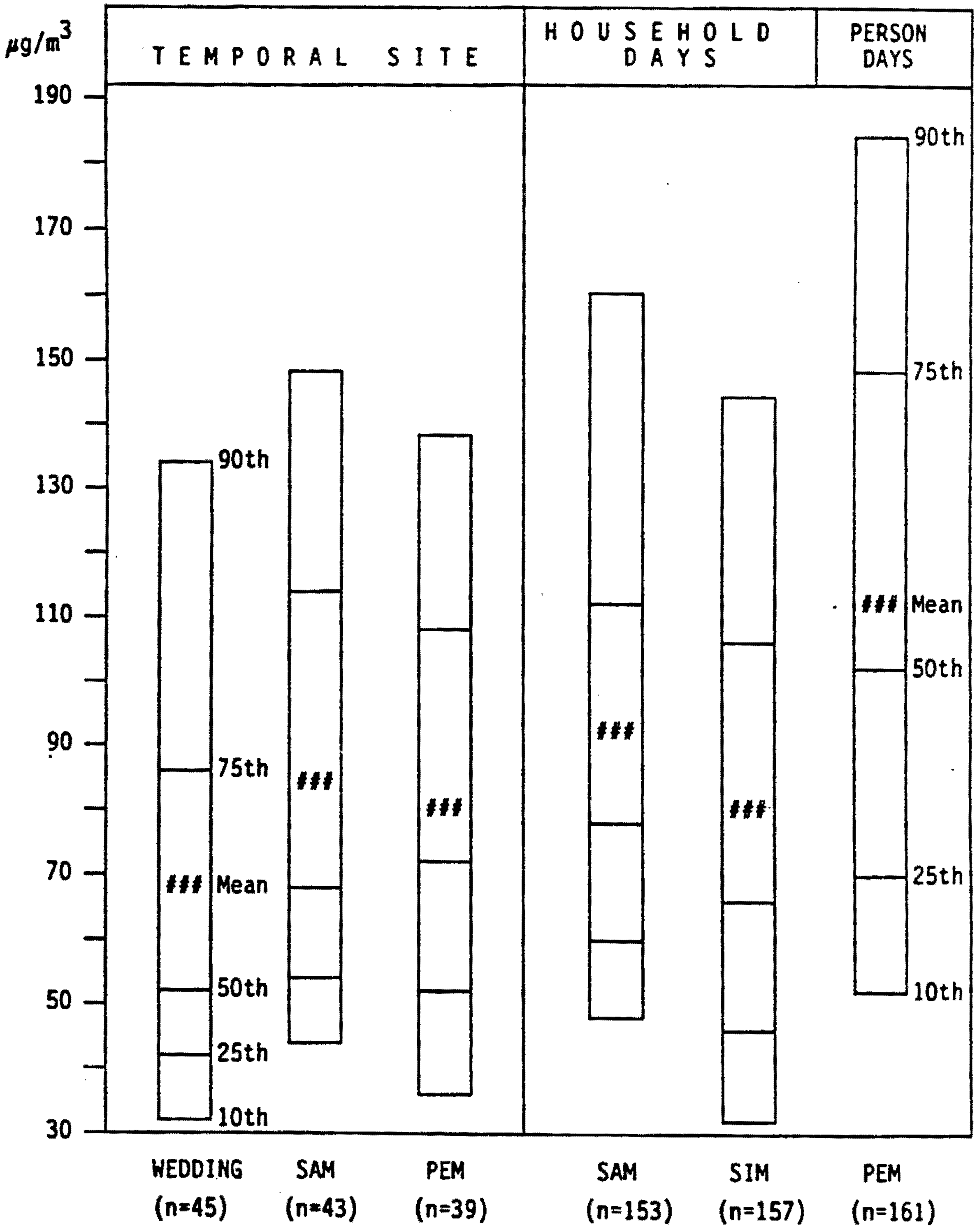


Figure 4-1. 24-Hour PM_{10} Distributions

Daytime outdoor levels ranged from 16 to 507 $\mu g/m^3$ with a median concentration of 84 $\mu g/m^3$. Nighttime indoor PM_{10} concentrations ranged from 14 to 180 $\mu g/m^3$ with a median concentration of 52 $\mu g/m^3$. Nighttime outdoor levels ranged from 14 to 223 $\mu g/m^3$ with a median concentration of 74 $\mu g/m^3$.

Ambient air concentrations of PM_{10} and $PM_{2.5}$ were measured throughout the course of the study at one fixed outdoor monitoring site in Riverside. A side-by-side trial, using the same personal and microenvironmental sampling systems that were used at homes, along with dichotomous and Wedding reference sampling methods, was conducted at this ambient air monitoring site. The ambient air monitoring site was designated as the "temporal site" in this study because air samples were collected by all four samplers for 96 consecutive 12-hour monitoring periods. The PEM (personal) sampling system mounted at the temporal site resulted in PM_{10} concentrations 8% higher than the dichotomous samplers; although this discrepency was found between samplers, it does not change the overall result of higher particulate levels found for personal exposure samples.

The personal exposures measured during this study would not have been predicted from ambient air or microenvironmental monitoring. The population's actual 24-hour PM_{10} exposure as measured by the personal monitors would have been underestimated by 30 to 40% based on ambient air levels measured by identical monitors located at the temporal site. The population's daytime median exposure would have been underestimated by 50% using ambient air measurements at the temporal site rather than personal exposure measurements.

Activity questionnaires and diaries were used to obtain information about activities or locations that could affect a person's exposure to particles during the monitoring period. Reported activities were examined for statistically significant correlations with personal and indoor air particle concentrations. Persons reporting daytime house work (indoor cleaning, cooking, etc.) were exposed to significantly higher PM_{10} concentrations than those reporting no house work. Daytime indoor PM_{10} and $PM_{2.5}$ levels were also significantly higher in homes with reported house work. Persons that did not go to work were exposed to significantly higher PM_{10} concentrations than persons reporting that they went to work. Many of the persons who did not go to work reported house work as an activity. The presence of tobacco smoke was associated with significantly higher daytime and nighttime indoor PM_{10} and $PM_{2.5}$ concentrations; personal exposure PM_{10} levels were significantly higher for those persons reporting exposure to tobacco smoke during the nighttime period only. No significant indoor or personal exposure concentration increases were associated with reported spraying of consumer products. Daytime personal and indoor particle concentrations were significantly higher in homes that <u>did not</u> report vehicle engines operated in attached garages. This surprising result may be related to other factors associated with owning a garage and suggests the need for analyses that attempt to deal simultaneously with several variables. No other activities or house conditions were significantly correlated with personal or indoor particle concentrations.

No strong correlations were observed between meteorological factors (temperature, dew point, wind speed) and particle concentrations. Ambient air PM_{10} and $PM_{2.5}$ concentrations did appear to have some dependence on wind speed and direction. Strong Santa Ana winds with gust above 40 knots were present during two time periods and were associated with high PM_{10} and low $PM_{2.5}$ levels. Visibility was improved with northerly winds (generally from the desert) in the 3 to 8 knot range when compared to westerly winds (from the Los Angeles basin) at 3 to 8 knots. Northerly winds at 3 to 8 knots also were associated with lower particle concentrations than were observed with westerly winds at 3 to 8 knots for both mean PM_{10} (42 vs 89 $\mu g/m^3$) and mean $PM_{2.5}$ (20 vs 50 $\mu g/m^3$) levels.

Additional source characterization will be performed by Harvard University based on both particle and elemental data. Results of this work will be reported in a separate document.

4.4.2 Elemental Concentration Distributions

Concentrations of selected elements were measured by X-ray fluorescence (XRF) analysis of all personal, indoor, outdoor, and dichotomous sample filters. Of 13 primary elements of interest, seven (silicon, aluminum, cobalt, iron, potassium, bromine, lead) were present at measurable levels on a sufficient number of samples for further data analysis. Seven elements of secondary interest (sulfur, zinc, chlorine, titanium, copper, strontium phosphorus) were also measurable on at least 50% of the personal sample filters. Three elements of primary interest (vanadium, selenium, nickel) were measurable on fewer than 20% of the personal, indoor, and outdoor filters. Two other elements (cadmium, arsenic) were also rarely measurable on dichot filters, as well as on the personal, indoor, and outdoor filters.

Relative elemental concentration distributions in personal, indoor, and outdoor air were similar to those observed for PM_{10} in most cases. Personal daytime concentrations of most elements were much higher than those measured indoors or outdoors. Personal nighttime concentrations were often higher than indoor levels but lower than outdoor levels. Sulfur was the most notable exception; it was primarily associated with particles smaller than 2.5 µm and the concentration distributions for personal, indoor, and outdoor locations were much more similar than those of any other element. Elements associated with soils (silicon, aluminum, calcium) were present at the highest concentrations, usually over 1000 ng/m^3 for PM_{10} samples. These three elements were usually found at much lower concentrations on the $PM_{2.5}$ samples. Potassium and sulfur concentrations were also often above 1000 ng/m^3. Lead was measured in a high percentage of samples, with mean concentrations ranging from

17 to 40 ng/m^3. Mean chlorine concentrations were observed above 200 ng/m^3, but these may not accurately reflect actual air concentrations since other data suggest losses due to volatilization during analysis or storage.

Mean element/particle mass ratios were calculated for the personal, indoor, and outdoor samples. Ratios for daytime personal samples were similar to those for indoor and outdoor samples. These data suggest that organic particles from people and their clothes were not responsible for most of the increase observed for personal exposure PM_{10} concentrations. Sulfur, unlike the other elements, had nearly identical concentration distributions for daytime personal, indoor, and outdoor samples. Further efforts are needed to determine whether the elevated daytime personal exposures are a result of a bias due to the design or operation of the personal sampling system or are a reflection of truly higher exposures to particles. If people are exposed to concentrations of particles higher than those measured with stationary monitors, then additional research is necessary to understand the mechanism that causes the elevated exposure and to determine the sources of the particles.

SECTION 5

STATISTICAL SAMPLING DESIGN/SAMPLE SELECTION

The use of a probability sample is one of several basic elements of the TEAM model. A probability sample is a sample for which every element of the target population has a known, nonzero probability of being included in the sample. Probability sampling methods were used to select the sample for both the PTEAM main study and this chemical characterization substudy. A probability sample design was used since it provides the only widely accepted basis for making inferences from a sample to a population (24,25). Probability samples also provide a defensible basis for calculating the standard errors of survey statistics.

Implementing a probability sampling design requires constructing a sampling frame containing all elements of the target population and assigning probabilities of selection to the listed units. Population units sampled in the PTEAM main study were person-days for personal exposure monitoring and household-days for indoor and outdoor microenvironmental monitoring. Household-days were also the population unit sampled for this chemical characterization study. The persons included in the PTEAM target population were the permanent residents of the city of Riverside, California (excluding the area around March Air Force Base, south of Allesandro Boulevard) who were at least 10 years of age at the time of the survey and who were not currently tobacco smokers. The households included in the target population were the residences of the eligible individuals. The days comprising the target population included all days in the field data collection period, September 22, 1990 through November 9, 1990. Justification for the choice of target area, the target time frame (Fall, 1990), the target age range, and the exclusion of smokers is given in Table 5-1.

TABLE 5-1. RATIONALE FOR STUDY DESIGN PARAMETERS

Parameters	Rationale
Target area	Riverside was selected as an area that met several important criteria. These included: - variable ambient aerosol levels - heterogenous housing - multiple pollutant sources - population representing a range of socioeconomic groups - state and local government cooperation
Time frame	Fall was selected based on fixed-site monitoring data suggesting that ambient air in Riverside has greatest range of particulate level during this season.
Age range	Children under the age of 10 were excluded since they would have difficulty wearing the personal exposure monitors and providing reliable time activity data.
Smoker Eligibility	Smoking was expected to overwhelm other particulate exposures, thus smokers were excluded as participants. Using this criterion for participant eligibility excluded homes where all members were smokers. Homes with at least one nonsmoking member were eligible.

Probability sampling methods were used to select a sample of person-days from the target population. The general approach for sample selection used a stratified, multistage area household sampling design. The sample was designed to allow field monitoring for approximately 175 nonsmoking individuals aged 10 or older and their associated residences. Two subsets of the residential population were then randomly selected for PAH and phthalate monitoring. The design was intended to yield approximately 60 homes where both indoor and outdoor microenvironmental monitoring would be performed and approximately 120 homes where indoor microenvironmental monitoring would be performed. These two subsets of homes were both designed to represent the 61,520 households in Riverside that makeup the study population.

Geographic areas were selected at the first stage of sampling. At the second stage, brief interviews were conducted for a sample of housing units within the selected areas to identify the household members eligible for the PTEAM study. These data were used by the interviewer to determine which individual, if any, to select from the household for personal PM_{10} exposure monitoring. People were selected so that overall person-level probabilities of selection were approximately equal, except for people who worked at least 30 hours per week outside the home and people who were exposed to passive smoking in their homes. These latter subpopulations were slightly oversampled to obtain sufficient sample sizes to support separate statistical analyses. Once eligible participants and their associated residences were identified, subsets of homes for indoor and outdoor PAH and phthalate monitoring were selected.

An overview of the sample selection process is given in Figures 5-1 and 5-2. Sample selection activities were performed as part of the main study. Complete details of the statistical sample design are provided in Volume 1 of the PTEAM final report (23).

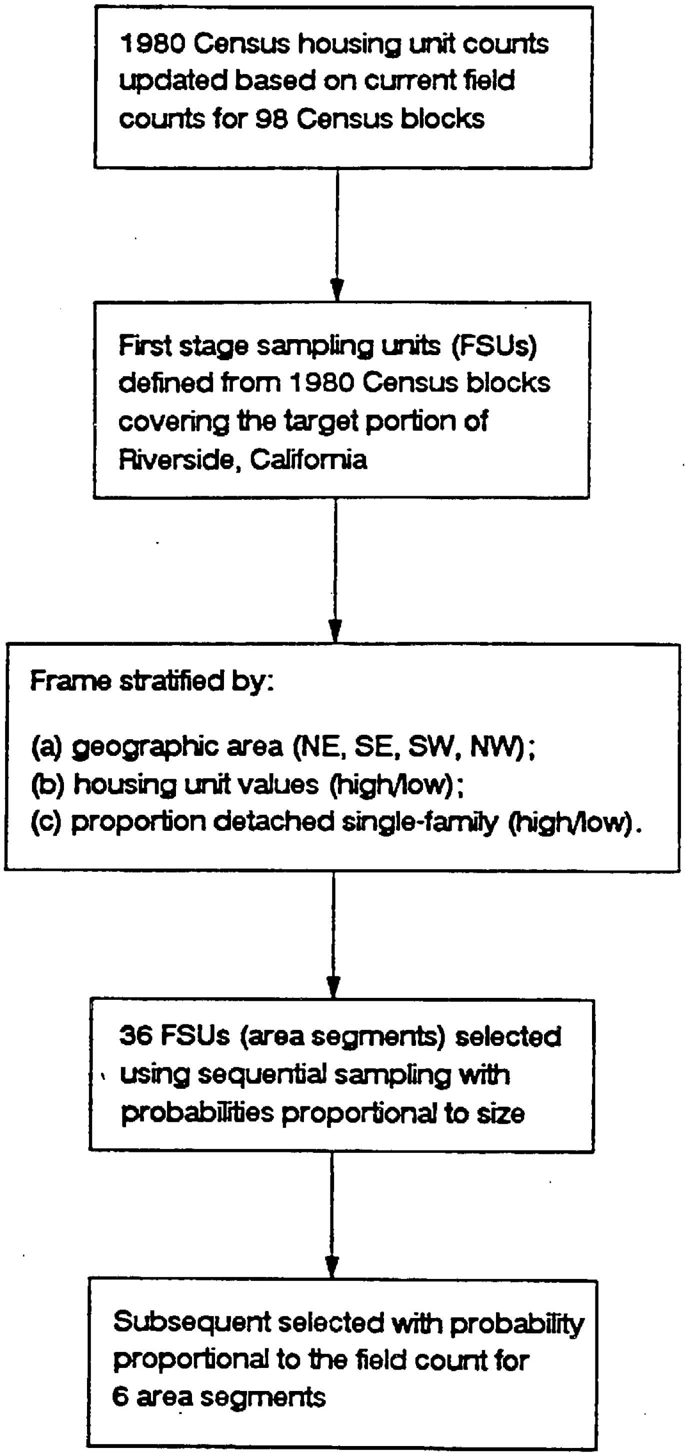
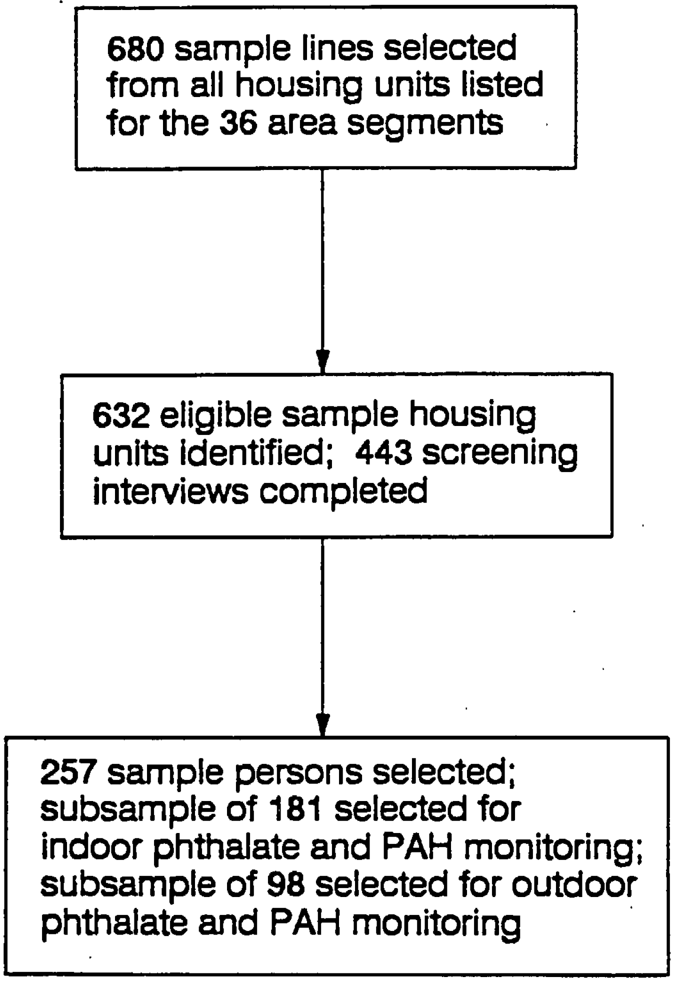


Figure 5-1. First-Stage Sample Selection Process



680 sample lines selected from all housing units listed for the 36 area segments

632 eligible sample housing units identified; 443 screening interviews completed

257 sample persons selected; subsample of 181 selected for indoor phthalate and PAH monitoring; subsample of 98 selected for outdoor phthalate and PAH monitoring

Figure 5-2. Second- and Third Stage Sample Selection Process

SECTION 6

SURVEY ACTIVITIES

All survey activities were performed as part of the PTEAM main study. These activities included development of questionnaires and related materials, hiring and training of field interviewers, screening participants, and enlisting eligible participants into the study. These activities were carefully coordinated with the field monitoring activities to ensure that reasonable schedules for sample collection in the field were maintained. A brief discussion of the activities is given below. More detailed information can be found in Volume 1 of the PTEAM Final Report (23).

6.1 DOCUMENTS

A series of questionnaires and related forms were developed concurrent with the study design activities. Table 6-1 lists the forms and their purposes. All questionnaires were modified several times and circulated for review. With each draft, reviewer comments were included and new drafts were prepared. The development of the documents continued in an iterative fashion until the design of the study and the data needs were finalized and all documents were approved by both ARB and EPA.

Most of the materials to be used in this study were tested in a series of focus group meetings held in Riverside. Emphasis was placed on the materials developed for the initial contacts with selected households. During the focus group meetings, versions of the mailing envelopes, lead letter and informational brochures were displayed and discussed. Incentive payments and interviewer scripts to be used during participant contacts were also evaluated. Respondents were asked what would make them participate and what might make them

TABLE 6-1. STUDY DOCUMENTS

Document	Purpose	Appendix
Participant Consent Forms	Obtain informed consent from participants. This is a requirement of all studies that involve human participants	A
Refusal Documentation and Conversion Form	Attempts to enlist participants and document refusals	B
Informational Package	Provide information to potential participants prior to asking them to participate	C
Field Interview Instruction Manual	Serve as a training and reference document for all survey activities	D[a]
Household Enumeration Questionnaire	List residents in a household, exclude non-eligible residents, guide interviewer through the participant selection process	E
Study Questionnaire	Obtain socio/economic information on participants, as well as information on the residence and work environment	F
Time/Activity Survey	Obtain information on locations and activities of participants; obtain information on potential sources for particulates and PAHs in the indoor and outdoor microenvironment	G

[a] Table of contents only

refuse. Almost all of the focus group participants expressed an interest in being part of the study. We used the information gathered during the meeting to revise the material and presentations used during the field effort.

Prior to field activities, personnel within EPA, ARB, and the city of Riverside were contacted to develop a public relations strategy. These activities included contacts with the media and a press release.

6.2 RECRUIT, HIRE, AND TRAIN FIELD STAFF

An experienced, well-trained staff of field interviewers led by an experienced supervisor is vital to the successful completion of an effort like PTEAM. The field supervisor was recruited with the assistance of RTI's Regional Survey Supervisor in Los Angeles. Field interviewers were then hired by the supervisor after interviewing applicants. Field interviewers were hired from a pool of applicants from Riverside and adjacent communities; included in the group of interviewers was an individual who spoke Spanish which allowed Spanish-speaking households to be contacted and recruited into the study.

Prior to field work interviewers were trained in all of the screening and recruitment procedures. A multi-day training session was held in the first week of September, 1990, with the staff receiving assignments and beginning work immediately after training was completed. Each interviewer received a copy of the Field Interviewer Instruction Manual to study. Classroom training consisted of a review of the study and the requirements for successful completion. Detailed instructions were provided for each step of the process. Each data collection instrument was reviewed on a question-by-question basis, then mock interviews as a group and individual practice interviews were performed in pairs.

Each interviewer was required to demonstrate adequate performance in all components of the study before leaving the training site and beginning to contact potential respondents. Project staff remained in Riverside for several days after training to assist the interviewers if problems arose, to assist the supervisor as she established the required flow of information, and to provide support to the field staff during the first few days of the effort.

6.3 SCREENING AND SAMPLE SELECTION

Each interviewer received an assignment consisting of several sampling areas grouped geographically to minimize travel time. The materials used for each segment of the assignment consisted of the segment sketch, listing forms created during the initial count and list process, and a set of labeled Household Enumeration Questionnaires (HEQs). Each questionnaire was uniquely labeled with address information and a line number corresponding to the segment listing form. Each document thus represented one selected housing unit which was contacted and worked to completion.

After planning their work load, the interviewers began to contact the housing units. Contact times were carefully chosen to maximize the probability of a successful contact on the first attempt. At the initial contact, interviewers attempted to complete the HEQ. This document created a roster of the residents in the household, and could only be completed by household residents who were at least 16 years of age.

Based on the results of the HEQ, interviewers immediately tried to enlist participants for field monitoring. To do this, the interviewer explained the study in detail, stressing the requirements of complete participation. Photographs of the monitoring equipment and typical placements were used as part of the explanation. After answering any questions about the study, the interviewer gave the participant consent form to the respondent and allowed him/her to read it or, if necessary, read it to him. The bilingual interviewer prepared a version of the consent form and other introductory material in Spanish, to be used as a guide, but not as a replacement for the original material. If they were at home, the interviewer asked to speak to them and began the recruiting process. If the respondent was not at home, or was unavailable at the time, the interviewer made a specific appointment for completing the enrollment and interview process.

After completing the informed consent process, the interviewer completed the Study Questionnaire with the respondent. The final step in the process was setting appointments for the monitoring team to come to the housing unit, set up the equipment, and subsequently retrieve it.

6.4 COMPLETING THE INTERVIEW AND SETTING APPOINTMENTS

Each housing unit assigned to an interviewer was worked until a final result code could be assigned and documented. Each interviewer reported progress on their assignment to the field supervisor during scheduled phone reports or routine meetings. The supervisor compiled the data on the screening effort and reported it electronically to survey staff at RTI or during routine phone calls. The progress reports were used to determine estimates of response rates and overall progress judged against the time available to complete the effort.

All documents collected by the field staff or the monitoring team were returned to RTI at the end of the field period. Consent forms and incentive receipts were separated from the other documents, sorted by participant identification number and filed in secured storage. Since these forms contain respondent names that were kept separate from other information to assure the confidentiality of the data. The remaining data collection instruments were batched for processing and edited for completeness, legibility, and internal consistency. After editing, documents were keyed and returned for storage. The keyed data underwent machine edits and were then made available for statistical analysis.

6.5 PERFORMANCE OF SURVEY METHODS

The overall response rate for the environmental measurements program is the product of the response rate for screening and for household/participant monitoring. For this study, 70% of the households contacted completed the screening interview and 69% of these agreed to participate in the monitoring for an overall response rate of 49%. As shown in Table 6-2, this response rate is low but consistent with other environmental monitoring programs. It is interesting to note, however, that the screening response rate was lower than most other studies, while the response rate for monitoring was higher. Procedures used here attempted to count and list households and enlist participants during a single time period that was coincident with monitoring. This was proposed as a less expensive approach. However, recent experiences with this study and the Woodland study suggest that lower response rates are achieved using this approach (21). For this study, low screening response rates were achieved as a result of not reaching all potential participants, since interviewers may have given priority to scheduling field monitoring at the expense of completing the screening interviews for all potential participants. This may have been a problem that is somewhat unique to Riverside where a number of residents commute very long distances and are only home very early in the morning or very late at night. If a higher response rate is required for future studies, then an approach that separates the screening and participation steps may be desirable.

TABLE 6-2. RESPONSE RATES ACHIEVED IN COMPARABLE EXPOSURE MONITORING STUDIES

Description of Study	Location	Season	Screening Response Rate	Number Monitored	Monitoring Response Rate	Overall Response Rate
Total Exposure Assessment for VOCs[a]	Bayonne, NJ	Fall '81	87%	154	55%	48%
Total Exposure Assessment for VOCs[a]	Elizabeth, NJ	Fall '81	84%	201	51%	43%
Total Exposure Assessment for VOCs[a]	Greensboro, NC	Spring '82	95%	24	80%	76%
Total Exposure Assessment for VOCs[a]	Devils Lake, ND	Fall '82	96%	24	67%	64%
Total Exposure Assessment for VOCs[a]	Los Angeles, CA	Winter '84	87%	117	64%	56%
Total Exposure Assessment for VOCs[a]	Antioch/Pittsburg, CA	Summer '84	89%	71	64%	57%
Total Exposure Assessment for VOCs[a]	Baltimore, MD	Spring '87	95%	155	62%	59%
CO Exposure Monitoring Study[b]	Washington, DC	Winter '83	70%	1,161	58%	41%
CO Exposure Monitoring Study[b]	Denver, CO	Winter '83	76%	485	43%	33%
Nonoccupational Pesticide Exposure Study[c]	Jacksonville, FL	Summer '86	74%	65	54%	40%
Nonoccupational Pesticide Exposure Study[c]	Jacksonville, FL	Spring '87	66%	53	73%	48%
Nonoccupational Pesticide Exposure Study[c]	Jacksonville, FL	Winter '88	81%	55	61%	49%
Nonoccupational Pesticide Exposure Study[c]	Springfield/Chicopee, MA	Spring '87	70%	49	55%	39%
Nonoccupational Pesticide Exposure Study[c]	Springfield/Chicopee, MA	Winter '88	84%	37	51%	43%
VOC, VVOC, and SVOC Exposure Study[d]	Woodland, CA	Spring '90	69%	128	74%	51%
Pilot PTEAM Study	Riverside, CA	Fall '90	70%	178	69%	49%

Legend: CO = Carbon monoxide; SVOC = Semivolatile organic compound; VOC = Volatile organic compound; VVOC = Very volatile organic compound.

[a] Reference 26
[b] Reference 27
[c] Reference 28
[d] Reference 21

SECTION 7

CHEMICAL SAMPLING AND ANALYSIS

7.1 FIELD MONITORING

Field monitoring was performed from September 22 to November 9, 1990. During that time period, monitoring for the PTEAM main study was performed in 178 homes. Monitoring for this chemical characterization component of the study was performed in 125 homes. Monitoring for both parts of the study was performed by two three-person field teams. A single person on each team was responsible for the monitoring associated with this chemical characterization substudy. As part of the PTEAM main study, a third team consisting of two individuals was used to place PFT emitters into each home for air exchange measurements. The interior dimensions of each home were measured by this third team and house volume was calculated; interior walls were considered nonexistent when making this calculation. Table 7-1 summarizes the schedule of activities in each home. Activities associated with this chemical characterization substudy are designated on the table. All other activities were performed as part of the PTEAM main study. The remainder of this section describes the activities that were associated with this chemical characterization study. All other activities are described in detail in Volume 1 of the PTEAM Final Report (23).

Indoor air samples for PAHs and phthalates were collected in the primary living area of each home selected for monitoring. For the purposes of this study, the primary living area was defined as the non-bedroom area where individuals spend most of their time, usually the living room or family room. Outdoor air samples were collected at a single outdoor site on the non-roadway side of the home. Where possible, the outdoor sampler was placed at least 15 feet away from the residence or other buildings, any roadways, parking lots, or known sources of PAHs or phthalates. Indoor air samples for PAHs and phthalates were

TABLE 7-1. TYPICAL APPOINTMENTS AND ACTIVITIES AT ONE PARTICIPANT'S HOME

Activity	Day	Nominal Time
INITIAL VISIT	Day 1	6:00 PM
- Harvard supervisor conducts this visit - Air exchange emitters deployed - House measured and house plan drawn - Sample collection locations determined and recorded - Appointment schedule confirmed with participant		
SET-UP VISIT	Day 2	8:30 PM
- Three-person sampling team conducts this visit - Set up and start indoor and outdoor particulate monitors - Set up and start personal particulate monitor - Deploy PFT collectors (CATS) for air exchange measurements *- Set up and start indoor and outdoor PAH/phthalate monitors - Discuss activity questionnaire with participant - Confirm remaining appointment times		
CHANGE-OUT VISIT	Day 3	6:30 PM
- Three-person sampling team conducts this visit - Remove used particulate filters, replace with new filters - Remove used CATS, replace with new CATS *- Remove used PAH/phthalate filters, replace with new filters - Administer activity questionnaire - Confirm final appointment time		
FINAL VISIT	Day 4	6:00 PM
- Three-person sampling team conducts this visit - Remove used particulate filters - Remove used CATS *- Remove used PAH/phthalate filters - Administer activity questionnaire - Pay participant $100 incentive, get signed receipt - Remove equipment from home		

* Activities associated with this chemical characterization substudy.

scheduled for collection at 125 homes. Paired indoor and outdoor samples were scheduled for 65 homes. Sample collection from each household was performed over two 12-hour periods intended to correspond with daytime and nighttime activities. Up to four homes were monitored per day.

In conjunction with field monitoring, questionnaire data were collected on the use of potential pollutant sources during the monitoring period, the activities of residents that may have affected indoor concentrations of the target chemicals during the monitoring period, and pertinent building characteristics of the residence. This information was collected at the end of each 12-hour period.

Several types of quality control samples were used throughout the study. Field blanks were used to assess contamination and/or interferences on field samples. These samples were unexposed sampling cartridges that traveled to the field site, then were returned to the laboratory and analyzed along with the field samples. Field controls were used to assess analyte recovery. To prepare these controls, XAD cartridges were spiked with known amounts of the 3- and 4-ringed PAHs and the phthalates; filters were spiked with the 5- to 7-ringed PAHs. As with the field blanks, field controls were shipped to the field, then returned and analyzed along with the samples. Quantitation limit (QL) samples were spiked with low levels of target chemicals, then treated exactly as field controls. The purpose of these samples was to estimate method quantifiable limits. Field samples were collected in duplicate and analyzed to evaluate precision. An urban dust standard reference material obtained from the National Institute of Standards and Technology was also used to evaluate method precision and accuracy.

Strict sample custody procedures were followed throughout the collection and analysis activities. Each sample was given a unique code to link that sample to the study participant and household, sample type, collection regime, etc. As part of our quality control procedures, sampling protocol/chain-of-custody forms were prepared for each sample collected. This form was used to track each sample from the time it was prepared until the data had been reduced and entered into a computer data base for statistical analysis.

Table 7-2 presents information on the number of samples scheduled, collected and analyzed. These data are provided for both the field and the QC samples.

7.2 MONITORING METHOD

7.2.1 Method Description

For air sampling, combined particulate and vapor phase PAHs and phthalates were collected using a 115-V AC medium-volume constant flow pump (Esoteric, Model SP-2511), coupled to a sampling cartridge containing a 21 mm quartz fiber filter backed by a 4.5 g bed of XAD-2 resin. During collection, sampling cartridges were wrapped in aluminum foil to protect them from light. Twelve hour samples were collected at a flow rate of approximately 17 L/min to provide a nominal sample volume of approximately 12 m^3. Flow rates at the cartridge inlet were measured before and after sample collection using calibrated rotometers with a fixed-orifice bypass tube.

As PAH samples were collected, they were stored in the field chilled and protected from light. All samples were shipped on dry ice to RTI via Federal Express. Immediately upon receipt at RTI, samples were checked for integrity (i.e., were containers broken, open, etc.; were samples identified correctly; what was the shipping date). Once it was established that samples had been received intact, they were logged-in. Chain-of-custody sheets were also checked and signed for each sample received. Samples were then stored at -20°C until extraction and analysis.

TABLE 7-2. STATUS OF SAMPLE COLLECTION, EXTRACTION, AND ANALYSIS ACTIVITIES

Sample Type	Number				
	Proposed	Scheduled	Collected	Extracted	Analyzed
Indoor air	240	250	228[a]	228	228
Outdoor air	120	130	96[a]	95[b]	95
Duplicates	18	24	18[a]	18	18
Field controls	18	18	18	18	18
QL samples[c]	7	7	8	8	8
Field blanks	18	18	18	18	18
NBS urban dust	7	7	7	7	7

[a] Indoor samples that were collected for less than 5 hours were not included. Outdoor samples that were collected less than 8 hours were not included.

[b] One sample dropped during extraction.

[c] Sample prepared and analyzed as a means for estimating method quantifiable limits.

All cartridge materials were rigorously cleaned prior to assembly and field deployment to ensure minimal background contamination. The XAD-2 sorbent material (Supelco, Inc.) was Soxhlet-extracted for 16 hours with methylene chloride. After extraction, residual methylene chloride was removed by placing the sorbent material in a vacuum oven at 55°C for 12 hours. Quartz fiber filters (Pallflex 2500QAT) were cut to a diameter of 17 mm and treated in a muffle furnace for 4 hours at 400°C to remove organic contaminants. All glassware was washed, heated to 400°C for four hours and rinsed with methylene chloride. All other cartridge materials were rinsed with methylene chloride and dried before assembly.

Prior to use in the field, a subset of assembled cartridge materials was extracted and analyzed by gas chromatography/electron capture detection (GC/ECD) to assure that background contamination was low. The greatest concern was contamination with the phthalate esters. Cartridges were considered acceptable only if levels of individual phthalates as measured by GC/ECD were less than 0.2 ng/cartridge.

PAHs and phthalates were recovered from the combined cartridge material by sonication extraction with 30 mL of methylene chloride for a 30-minute period. The solvent extract was separated from the cartridge material by filtering through silanized glass wool. The filtered extract was then concentrated to ~1 mL using nitrogen blowdown. The extract was solvent exchanged into toluene and further concentrated to 0.1 mL.

Deuterated surrogate standards were added to samples immediately prior to extraction to monitor overall method performance. External quantitation standards were added to sample extracts immediately prior to final concentration and analysis. Fluoranthene-d_{10}, chrysene-d_{12}, benzo[e]pyrene-d_{12}, and di-n-octylphthalate-d_4 were used as the surrogate standards. Acenaphthene-d_{10}, 9,10-dichloroanthracene, and perylene-d_{12} were used as external quantitation standards.

Sample extracts were analyzed by direct liquid injection capillary GC/MS. A 1-µL aliquot of the sample extract was injected using a split/splitless injection technique. Analytes separated on the GC column were introduced to a quadrupole mass spectrometer operating with electron ionization in the selected ion monitoring (SIM) mode. Sample constituents were characterized and quantitated by measuring ions characteristic of the target chemicals. Instrumental operating parameters are described in Table 7-3.

Prior to analysis, the GC/MS system was calibrated by analyzing the standards shown in Table 7-4. Concentrations of the target PAHs and phthalates were chosen to bracket the concentration distributions expected in air samples. Generally, calibrations were performed using the GC/MS peak area of the parent and parent-plus-one ions for each analyte. Calibration ions are listed in Table 7-5. For PAHs with no other chemical substituents, the parent ion was selected as the primary ion because it is usually the ion with the greatest relative abundance for PAHs. The parent-plus-one ion was included to verify compound identification.

Results of individual calibration analysis were used to generate relative response factors (RRF) using the following equation:

$$RRF_t = \frac{A_t / C_{std}}{A_{std} / C_t}$$

where: A = system response (integrated peak area)

C = concentration in calibration standard (ng/mL)

t = analyte

std = external quantitation standard.

TABLE 7-3. GC/MS OPERATING PARAMETERS FOR ANALYSIS OF PAHs AND PHTHALATES

Column Type:	30 m, DB-5, 0.25 mm i.d., 0.1 µm film
Run Type:	Electron ionization; selected ion monitoring
Injection Type:	Splitless/Split (0.5 min)
Injection Temperature:	300°C
Interface Temperature:	300°C
Source Temperature:	200°C
GC Program:	Initial temperature = 100°C Initial program rate = 15°C/min to 130°C Program rate = 3°C/min Final temperature = 300°C Final hold time = 20 minutes
Instrument:	Hewlett Packard 5988A
Multiplier Voltage:	2000[a]
Emission Current:	~300 mA[a]
Dwell Time:	75-250 msec

[a] A typical value.

TABLE 7-4. CALIBRATION STANDARDS FOR PAH AND PHTHALATE ANALYSIS

	Concentration (pg/uL)			
Compound	0.2 X	0.5 X	1 X	2 X
PAHs				
Acenaphthylene	198	495	990	1980
Phenanthrene	490	1,225	2,450	4,900
Anthracene	26.3	65.8	132	263
Fluoranthene	215	538	1,080	2,150
Pyrene	112	280	560	1120
Benzo[a]anthracene	183	45.8	91.5	183
Chrysene	18.4	46.0	92.0	184
Benzo[k]fluoranthene	183	45.8	91.5	199
Benzo[e]pyrene	18.8	47.0	94.0	188
Benzo[a]pyrene	10.6	26.5	53.0	106
Indeno[1,2,3-cd]pyrene	11.9	23.8	47.5	95
Benzo[ghi]perylene	24.5	61.2	123	245
Coronene	16.2	40.5	81.0	162
Phthalates				
Diethylphthalate	1000	2500	5000	10000
Di-n-butylphthalate	1000	2530	5050	10100
n-Butylbenzylphthalate	1010	2530	5050	10100
di-n-octylphthalate	1000	2500	5000	10000
Di-2-ethylhexylphthalate	996	2488	4980	9950
Surrogate Standards				
Fluoranthene-d_{10}	103	258	515	1030
Chrysene-d_{12}	19.9	49.8	99.5	199
Benzo[e]pyrene-d_{12}	20.5	51.3	103	205
Di-n-octylphthalate-d_4	101	253	505	1010
External Quantitation Standards				
Acenaphthene-d_{10}	732	732	732	732
9,10-Dichloroanthracene	193	193	193	193
Perylene-d_{12}	96.6	96.6	96.6	96.6

TABLE 7-5. IONS USED FOR QUANTITATION AND VERIFICATION OF PAHs AND PHTHALATES DURING GC/MS ANALYSIS

Chemical	Quantitation Ion m/z[a]	Verification Ion m/z
PAHs		
Acenaphthylene	152	153
Phenanthrene	178	179
Anthracene	178	179
Fluoranthene	202	203
Pyrene	202	203
Benzo[a]anthracene	228	229
Chrysene	228	229
Benzo[k]fluoranthene	252	253
Benzo[e]pyrene	252	253
Benzo[a]pyrene	252	253
Indeno[1,2,3-cd]pyrene	276	277
Benzo[ghi]perylene	276	277
Coronene	300	301
Phthalates		
Diethylphthalate	149	177
Di-n-butylphthalate	149	243
n-Butylbenzylphthalate	149	91
Di-n-octylphthalate	149	167
Di-2-ethylhexylphalate	149	167

[a] m/z = Mass-to-charge ratio.

Average RRFs were then calculated using results from each calibration standard. Instrumental calibration was considered acceptable if the percent relative standard deviation of the average RRF value was less than 25 for each of the target PAHs and phthalates.

During sample analysis, two performance checks were made on the analytical system at the start of each day. First, the tune compound, perfluorotributylamine, was introduced into the mass spectrometer ionization source. All characteristic fragment ions were required to be present in the correct relative abundance before proceeding with any further analyses. Second, a mid-level calibration standard (0.5X standard, Table 7-4) was analyzed and RRF values calculated for each target PAH. Each analyte was considered "in control" if the RRF values calculated for the primary ion were within ± 25% of the mean RRF for that analyte. No corrective action was required if benzo[a]pyrene was "in control" and no more than two other analytes were "out of control". If acceptable performance was not demonstrated, a new calibration curve was generated.

Analyte amounts in sample extracts (T) were calculated as:

$$T(ng) = \frac{A_t \cdot C_{std} \cdot V_e}{A_{std} \cdot RRF_t}$$

where V_e is the final extract volume. Since the volume of air collected for a given sample was accurately known and the quantity per cartridge was determined, the concentration in (ng/m^3) ambient air was calculated as

$$ng/m^3 = \frac{T_s - T_{bkg}}{m^3}$$

where: T_s = Analyte amount found in sample (9ng)

T_{bkg} = mean background values on the field blank cartridges (ng)

m^3 = sample volume in cubic meters.

Data on the analyte amounts in each sample were transferred to electronic files where all additional calculations were made. These files then became part of the data base for statistical analysis.

7.2.2 Method Evaluation

7.2.2.1 Field Performance

The pumping system used to collect the PAH and phthalate samples was a Model SP-2511 made by Esoteric Systems, Inc. (Thousand Oaks, CA). This system was custom designed and built to RTI's specifications as a compact, very quiet, constant flow pump. The pump operates on standard household current of 115 VAC and requires less than 1.8 amps of current. It has outside case dimensions of 14.6 in x 14.2 in x 9.4 in. The case is weather resistant making it suitable for use in indoor or outdoor environments. Maximum flow capacity is 25 L/min with a nominal flow rate of 17 L/min when the PAH sampling cartridge is in place. A cartridge with 4.5 g of XAD sorbent usually resulted in a pressure drop of less than 7 in Hg. A pressure transducer and electronic circuitry are used to provide constant flow during sample collection. Actual flow rates were measured during field monitoring at the time of sampler deployment and retrieval using a calibrated rotameter. The temperature operating range for the pumps is approximately -10° to +50°C. The pumps are constructed using a minimum amount of adhesives and other materials that out-gas contaminants in order to reduce the potential for contaminating the area being sampled. Laboratory tests were performed prior to field monitoring which verified that out-gassing of PAHs or phthalates should not be a substantial problem during field monitoring. Low levels of di-n-butylphthalate, di-2-ethylhexylphthalate and phenanthrene were found during testing, but these were substantially lower than levels measured in air samples.

Sample collection time is indicated by a digital elapsed time display. An automatic low flow shut-off was incorporated as a safety feature to prevent the pumps from overheating and causing a potential fire hazard during monitoring. The shut-off mechanism is activated if the tubing is crimped, if a restriction occurs that causes the flow to drop below a predetermined low flow set-point or if a drop in power operating the pump occurs. In the event of an automatic shut-off, the elapsed collection time remains displayed. Noise levels produced by the pump during operation are very low, making it ideal for indoor sampling. Noise levels have been measured as less than 50 db at 1 meter during laboratory testing.

During this study, measured flow rate variability was less than 0.5 L/min over the 12-hour monitoring period for nominal sample flow rates of 17 L/min. The pumps were very reliable except in certain cases where the incoming line voltage to the pump dropped substantially. In these cases, depending on the duration and severity of the voltage drop, the pump either shut-off but left the elapsed time remaining or completely turned the unit and display off. Subsequent to this study, the pumps have been modified with a battery backup that holds the charge to the pump and allows the pump to restart after short duration voltage drops. If the drops are longer than 5 minutes, the pump will not restart, but the sampling time will be recorded.

Table 7-6 provides information on the number of samples that were not collected because of the pump shut-off. Taking into account all reasons for losses, 89% of the scheduled indoor samples and 73% of the scheduled outdoor air samples were collected for at least 8 hours during the 12-hour monitoring period.

7.2.2.2 Instrumental Performance

GC/MS system performance was acceptable throughout the sample analysis period. During the initial calibration, linearity over the concentration range of the standards was demonstrated for all of the PAHs. The percent relative standard deviation of the average RRF values was less than ± 25% for each of the target PAHs. For BaP, linearity down to 10.6 pg/uL (lowest calibration standard) was demonstrated. This concentration of BaP in a sample extract would be equivalent to an air concentration of 0.08 ng/m^3 assuming a 12.5 m^3 sample volume. This air concentration is well below the 0.3 ng/m^3 level that Offerman and Daisey (15) have suggested is required to cause a 10^{-6} excess cancer risk over a 70-year exposure period.

All daily performance checks on the GC/MS system indicated "in-control" instrumental performance during the sample analysis period. At no time during sample analysis did the RRFs for any of the target chemicals fail the ± 25% RSD "in control" criteria.

7.2.2.3 Method Performance

Several types of quality control (QC) samples were prepared and analyzed.

- Field controls (FC) were sample cartridges spiked with target analytes at known concentrations. The 3- and 4-ringed PAHs and the phthalates were spiked as solutions onto the XAD-2 resin material. The 5- to 7-ringed PAHs were spiked as solutions directly onto the filter. These samples were taken to the field and treated exactly as field samples, but were not exposed.

TABLE 7-6. SAMPLE COLLECTION RATE

Samples	Number		Percent[a]	
	Indoor	Outdoor	Indoor	Outdoor
Scheduled	265	139	100	100
Not attempted	0	0	0	0
Collected for entire monitoring period (12 hours)	232	101	87.5	72.7
Collected for 8 to 12 hours	3	1[b]	1.1	0.8
Collected for 5 to 8 hours	7	9[b]	2.6	6.5
Collected for less than 5 hours	11[b]	14[b]	4.2	10.1
Power/pump failure - no displayed time	12[b]	14[b]	4.5	10.1
Not collected for other reason	0[b]	0[b]	0	0

[a] Percent of samples scheduled.
[b] Not used for data analysis.

- Field blanks (FB) were unspiked cartridges. These samples were taken to the field and treated exactly as field samples, but were not exposed.
- Filter controls were filters embedded with a known concentration of NIST urban dust certified for PAH concentrations. These samples were prepared and stored in the laboratory. They were then processed and analyzed with the field samples.
- Method controls (MC) were extraction solvent spiked with target analytes then processed and analyzed with the field samples.
- Method blanks (MB) were unspiked extraction solvent processed and analyzed with the field samples.
- Quantitation limit samples were identical to field controls but were spiked with one-tenth the amount of target analytes. These samples were used to estimate method quantifiable limits.
- Duplicates were field samples collected at the same time and location, then processed and analyzed separately to assess precision.

Method performance data based on the results of these QC samples are presented below.

Field and method blanks were used to assess background contamination. Results for these analyses are summarized in Table 7-7. Data show low levels of PAHs for all blanks, indicating that background contamination was not a problem. Highest amounts were found for the low molecular weight PAHs; but these levels are low compared to the levels measured in air samples. For the phthalates, rather high amounts of diethyl-, di-n-butyl-, and di-2-ethylhexylphthalate were found on both types of blanks samples with slightly higher amounts found on field blanks. Highest amounts were reported for diethylphthalate with 266±368 ng found on field blanks. Although amounts found in both the method blanks

TABLE 7-7. RESULTS OF ANALYSIS OF BLANK SAMPLES

Compound	Mean Amount ± S.D. (ng) Field Blank (n = 14)[a]	Mean Amount ± S.D. (ng) Method Blank (n =16)
PAHs		
Acenaphthylene	1.2 ± 4.8	ND[b]
Phenanthrene	9.4 ± 13	2.1 ± 1.1
Anthracene	ND	ND
Fluoranthene	1.7 ± 4.9	0.3 ± 0.2
Pyrene	1.5 ± 2.6	0.3 ± 0.9
Benzo[a]anthracene	0.1 ± 0.3	ND
Chrysene	0.1 ± 0.3	ND
Benzo[k]fluoranthene	0.1 ± 0.4	ND
Benzo[e]pyrene	0.0 ± 0.1	ND
Benzo[a]pyrene	0.0 ± 0.1	ND
Indeno[1,2,3-cd]pyrene	0.1 ± 0.3	0.1 ± 0.4
Benzo[ghi]perylene	0.2 ± 0.7	0.5 ± 0.8
Coronene	0.2 ± 0.5	0.5 ± 1.0
Phthalates		
Diethylphthalate	266 ± 368	220 ± 330
Di-n-buthylphthalate	110 ± 66	100 ± 53
Butylbenzylphthalate	15 ± 14	9.1 ± 6.8
Di-n-octylphthalate	8.2 ± 1.5	2.6 ± 3.5
Di-2-ethylhexylphthalate	94 ± 78	64 ± 29

[a] Number of samples.
[b] No instrumental response.

and field blanks were higher for the phthalates than for the PAHs, they were still approximately an order of magnitude lower than amounts found in indoor air samples. Accuracy of the monitoring method for PAHs and phthalates was evaluated using control samples spiked with standard solutions and filters spiked with NIST certified urban dust. At the outset of this study, it was felt that chemicals spiked directly onto the XAD resin would not mimic the behavior of chemicals on particles collected on the filter. As a consequence, field controls for the higher molecular weight, particle bound PAHs, (including BaP), were prepared by spiking solutions of these chemicals directly onto the filter. Results of field control analyses indicated chemicals spiked in this manner are subject to volatilization and degradation losses. These losses should not be encountered when the chemical is attached to particles on the filter. Hence, field controls for the 5- to 7-ringed PAHs did not effectively represent chemical behavior during collection, storage, and analysis and therefore this method of preparing controls was not considered valid. A review of the literature and contact with other individuals performing PAH monitoring substantiated this conclusion. A more detailed discussion of this problem is given in Appendix H. As an alternate approach, we investigated using filters embedded with NIST certified urban dust as laboratory control samples that would mimic the behavior of particle-bound PAHs.

Table 7-8 gives results for the method and field control samples analyzed during this study. Table 7-9 gives results for the NIST urban dust spiked controls. Results showed recoveries greater than 70% for target PAHs spiked onto XAD cartridges. Recoveries of the 5-, 6-, and 7-ring PAHs from the field controls were not calculated since, as discussed above, the method for preparing these controls was not considered valid. Recoveries of PAHs from NIST certified urban particulate were also greater than 70%, although recoveries for indeno[1,2,3-cd]pyrene were high (126%). For both types of control samples, BaP gave mean

TABLE 7-8. RESULTS OF METHOD CONTROL (MC) AND FIELD CONTROL (FC) ANALYSES FOR PAHs AND PHTHALATES

Compound	Spiked		% recovery + S.D.[a]	
	ng	ng/m³[b]	MC (n = 25)[c]	FC (n = 14)
PAHs				
Acenaphthylene	100	8.0	84 ± 11	86 ± 15
Phenanthrene	250	20	90 ± 14	86 ± 8
Anthracene	13	1.04	71 ± 25	75 ± 25
Fluoranthene	100	8.0	104 ± 15	95 ± 10
Pyrene	53	4.2	102 ± 13	96 ± 22
Benzo[a]anthracene	9.5	0.76	93 ± 15	83 ± 16
Chrysene	9.5	0.76	100 ± 16	81 ± 11
Benzo[k]fluoranthene	10	0.80	111 ± 13	NA[d]
Benzo[e]pyrene	10	0.80	90 ± 10	NA
Benzo[a]pyrene	5.5	0.44	95 ± 19	NA
Indeno[1,2,3-cd]pyrene	4.7	0.38	119 ± 29	NA
Benzo[ghi]perylene	12	1.0	101 ± 19	NA
Coronene	9.5	0.76	99 ± 30	NA
Phthalates				
Diethylphthalate	500	40	56 ± 44	65 ± 66
Di-n-butylphthalate	510	41	113 ± 26	110 ± 39
Butylbenzylphthalate	510	41	90 ± 25	80 ± 26
Di-n-octylphthalate	500	40	105 ± 27	87 ± 17
Di-2-ethylhexylphthalate	500	40	76 ± 24	81 ± 75

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[a] All recoveries corrected for background on field blanks.
[b] Equivalent air concentration assuming a sample volume of 12.5 m³.
[c] n = number of samples.
[d] PAHs spiked directly on filter; not considered valid field controls.

TABLE 7-9. RESULTS OF ANALYSES FOR LABORATORY CONTROLS SPIKED WITH NIST STANDARD REFERENCE MATERIAL

	Spiked[a]		% Recovery + S.D.
Compound	ng	ng/m[3b]	(n = 6)
Fluoranthene	29	2.3	72 ± 14
Benzo[a]anthracene	12	0.96	61 ± 09
Benzo[a]pyrene	13	1.0	91 ± 17
Indeno[1,2,3-cd]pyrene	15	1.2	126 ± 33
Benzo[ghi]perylene	20	1.6	108 ± 09

[a] Mean amounts based on spiked NIST SRM 1649.

[b] Equivalent concentration assuming a sample volume of 12.5 m^3.

recoveries greater than 90%. Calculated concentration for field samples were <u>not</u> corrected for recovery.

Recovery of the phthalates from the field controls was more variable than for the PAHs. This was most apparent for diethylphthalate, di-n-butylphthalate, and di-2-ethylhexylphthalate. These results are probably a result of high and variable background contamination present in the field controls. The spiking levels for these chemicals was close to the calculated quantitation limit thus higher variability would be expected. Again, the spiking levels for the controls are substantially lower than the levels actually found on indoor air samples.

Accuracy of the monitoring methods was also evaluated by spiking each sample and QC sample with deuterated surrogate standards prior to extraction then measuring the amount found in each sample extract. Essentially, these surrogates represent the range of target PAHs and are designed to monitor performance of the extraction and analysis procedure in each sample. Data in Table 7-10 show acceptable recovery (> 70%) and reproducibility for the four surrogate standards. Benzo[e]pyrene-d_{12} is a 5-ringed PAH that should effectively mimic the behavior of BaP during extraction and analysis. Results for this chemical showed recoveries of 89 ± 23% for analyses performed during the study.

Method precision has been estimated based on results of analysis of duplicate sample pairs. Data in Table 7-11 show the percent relative mean deviations (% RMD) for measured air concentrations in duplicate samples. Precision between duplicate samples was generally very good. Median % RMD values for duplicate samples that contained measurable concentrations were less than 12% for all target chemicals with the exception of di-n-octylphthalate. This chemical was only detected at very low levels in all samples. Mean and median % RMD values for BaP were 8.9% and 3.0%, respectively.

TABLE 7-10. REPORTED RECOVERIES OF SURROGATE PAHs FROM FIELD SAMPLES, CONTROLS, AND BLANKS

	Spiked (ng)	% recovery ± S.D. (n = ~400)
Fluorene-d_{10}	103	87 ± 26
Chrysene-d_{12}	19.9	89 ± 20
Benzo[e]pyrene-d_{12}	20.5	89 ± 23
Di-n-octylphthalate-d_4	101	88 ± 24

TABLE 7-11. PERCENT RELATIVE MEAN DEVIATION (% RMD) FOR DUPLICATE SAMPLES[a]

		% RMD[b]	
Compound	n[c]	Mean	Median
Target PAHs			
Acenaphthylene	9	15	8.7
Phenanthrene	14	8.8	6.1
Anthracene	11	8.7	7.6
Fluoranthene	12	7.3	4.4
Pyrene	14	7.4	5.6
Benzo[a]anthracene	6	13	10
Chrysene	10	11	8.3
Benzo[k]fluoranthene	8	16	6.8
Benzo[e]pyrene	8	8.1	3.5
Benzo[a]pyrene	7	8.9	3.0
Indeno[1,2,3-cd]pyrene	8	16	10
Benzo[ghi]perylene	11	15	8.6
Coronene	9	17	10
Target Phthalates			
Diethylphthalate	10	11	10
Di-n-butylphthalate	11	7.1	3.9
Butylbenzylphthalate	11	12	4.8
Di-2-ethylhexylphthalate	11	8.0	7.3
Di-n-octylphthalate	3	26	17

[a] If both quantifiable.

[b]

$$\%RMD = \frac{|C_s - C_b|}{(C_s + C_b)/2} \times 100\%$$

where C_s and C_b are the measured concentrations in the field sample and the duplicate sample, respectively.

[c] Number of paired samples.

Finally, method quantifiable limits (MQL) were calculated by spiking cartridges with low levels of all target compounds. These cartridges were transported to the field site, returned, and analyzed along with the sample cartridges. MQLs were then calculated using the following equation (29):

$$MQL(ng) = S.D. \ x \ t_{0.99}$$

where S.D. = the standard deviation around the mean ng for the analysis of the eight fortified cartridges.

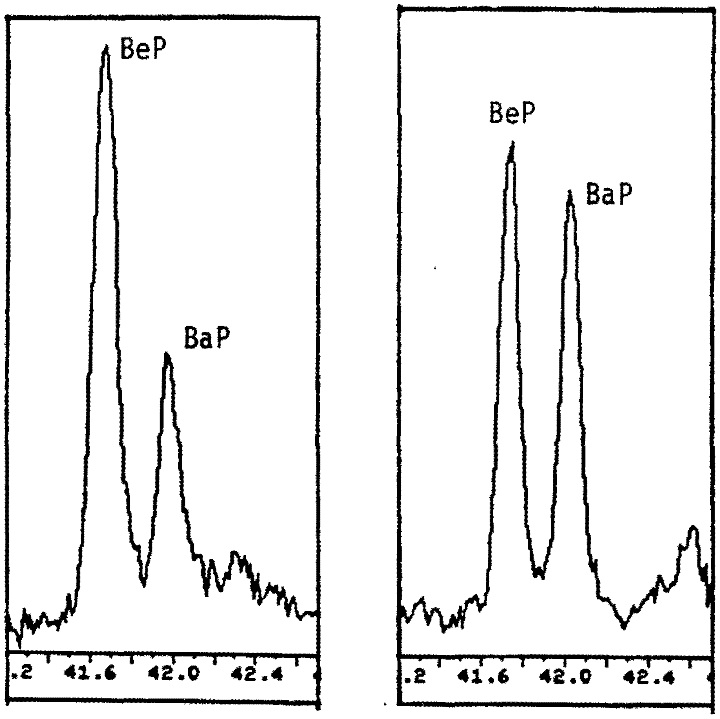
$t_{0.99}$ = students one-tailed t-statistic at the 99% confidence level with seven degrees of freedom.

For a number of chemicals, the standard deviation of the measured amounts were very low. This resulted in calculated MQL values that were unrealistically low based on the signal to noise ratio of the GC/MS response. Where this was the case, a conservative approach was taken and the MQL was calculated using the concentration of the lowest calibration standard. Figure 7-1 gives GC/MS chromatograms of BaP for a standard and a sample with concentrations at the MQL.

Results of MQL determinations are given in Table 7-12. Offerman and Daisey (4) have suggested that a monitoring method for PAHs should be sufficiently sensitive to detect BaP at an air concentration of 0.3 ng/m^3. This is the concentration for which it has been estimated that the risk of cancer for lifetime exposure is less than 10^{-6}. For this study, the median MQL for BaP was 0.08 ng/m^3 indicating that the method is sufficiently sensitive to obtain data useful in exposure and risk assessments.

7.2.2.4 Matrix Effects

Analytical results for the field samples were evaluated to determine if interferences or other matrix effects prevented quantitation of the target PAHs and phthalates. Table 7-13



Standard

Sample

Figure 7-1. GC/MS Chromatograms of Benzo[a]pyrene (BaP) and Benzo[e]pyrene (BeP) Present in a Sample and a Standard as the Estimated Quantitation Limit (~10 pg injected on column; 1 ng/sample).

TABLE 7-12. ESTIMATED MEDIAN METHOD QUANTIFIABLE LIMITS (MQL)

	MQL	
Compound	ng/sample	ng/m^{3a} (n = 339)
PAHs		
Acenaphthylene	12	1.0
Phenanthrene	33	2.8
Anthracene	2.1	0.18
Fluoranthene	13	1.1
Pyrene	6.8	0.57
Benzo[a]anthracene	1.3	0.11
Chrysene	1.1[b]	0.090
Benzo[k]fluoranthene	1.0[b]	0.080
Benzo[e]pyrene	1.0[b]	0.080
Benzo[a]pyrene	1.0[b]	0.080
Indeno[1,2,3-cd]pyrene	2.7	0.22
Benzo[ghi]perylene	1.8	0.15
Coronene	2.9	0.24
Phthalates		
Diethylphthalate	950	80
Di-n-butylphthalate	170	14
Butylbenzylphthalate	60	5.1
di-n-octylphthalate	38	3.2
Di-2-ethylhexylphthalate	290	24

[a] Calculated as ng/sample ÷ sample volume; median MQL calculated for field samples. Ranges for MQL values are given in Table 8-2.

[b] Calculated from lowest point on calibration curve; since other methods gave artificially low values.

TABLE 7-13. SAMPLES NOT QUANTITATED DUE TO MATRIX EFFECTS DURING ANALYSES

	Samples			
	Indoor (n = 228)[a]		Outdoor (n = 95)	
Compound	Number	%	Number	%
PAHs				
Acenaphthylene	6	2.6	1	2.1
Phenanthrene	1	0.4	2	0
Anthracene	6	2.6	0	0
Fluoranthene	2	0.9	0	0
Pyrene	1	0.4	0	0
Benzo[a]anthracene	16	7.0	0	0
Chrysene	15	6.5	0	0
Benzo[k]fluoranthene	144	63	64	67
Benzo[e]pyrene	8	3.6	0	0
Benzo[a]pyrene	6	2.6	0	0
Indeno[1,2,3-cd]pyrene	11	4.8	3	3.2
Benzo[ghi]perylene	2	0.9	1	1.1
Coronene	0	0	0	0
Phthalates				
Diethylphthalate	1	0.4	0	0
Di-n-butylphthalate	1	0.4	0	0
Butylbenzylphthalate	0	0	0	0
Di-2-ethylhexylphthalate	0	0	0	0
Di-n-octylphthalate	8	3.6	0	0

[a] Number of samples.

summarizes information on the number and percentage of indoor and outdoor air samples where quantitative measurements could not be made. With the exception of benzo[k]-fluoranthene (BkF), interferences were not a problem. For BkF a large closely eluting peak caused analytical interferences. Based on previous reports, the peak probably consists of a mixture of benzo[i]fluoranthene and benzo[j]fluoranthene (6). Only at high BkF concentrations could BkF and the interfering peak be resolved and quantitation performed. In the remaining samples, BkF was reported as detected but was not quantitated.