Indoor Air, 4, 497-512 (1991)

A Pilot Study to Measure Indoor Concentrations and Emission Rates of Polycyclic Aromatic Hydrocarbons

F.J. Offermann[1], S.A. Loiselle[1], A.T. Hodgson[2], L.A. Gundel[2] and J.M. Daisey[2]
Indoor Environmental Engineering, San Francisco, USA

Abstract

Sampling and analytical methods for gas- and particulate-phase polycylic aromatic hydrocarbons (PAH) in indoor air were evaluated in a controlled field study. Using 12-h, 25-m³ samples, gas-phase PAH were collected on XAD-4 resin and analyzed by GC-MS, and particulate-phase PAH were collected in filters and analyzed for by HPLC with fluorescence detection. Tests were conducted in homes and office buildings without active combustion sources and with gas stoves, wood stoves and cigarette smoking as controlled sources. Indoor concentrations, outdoor concentrations and air-exchange rates were simultaneously measured. The precisions of the concentrations were evaluated using collocated sample pairs collected indoors and outdoors. Net emission rates were calculated for the gas-phase PAH. Net emissions of these compounds were measured in buildings without active combustion sources. Environmental tobacco smoke was identified as a significant source of both gas- and particulate-phase PAH.

KEY WORDS:
Air-exchange rate, Analytical precision, Emission rate, Environmental tobacco smoke, Gas range, Indoor air, Polycyclic aromatic hydrocarbons, Wood stove.

Manuscript received: 27 November 1991
Accepted for publication: 27 November 1991

[1] Indoor Environmental Engineering, 2209 Pine Street, San Francisco, CA 94115, USA
[2] Indoor Environment Program, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, USA

Introduction

A number of polycyclic aromatic hydrocarbons (PAH), including some nitrogen-heterocyclic analogues (aza-arenes) and nitro-derivatives, have been shown to be carcinogenic in animals (NAS, 1983). Others are biologically active as co-carcinogens and tumor promoters (USDHHS, 1982). Workers exposed to mixtures of these compounds from industrial processes have been found to have a higher risk of developing lung cancers (NAS, 1983). High exposures to PAH and aza-arenes have recently been reported for a population in China with high lung cancer rates (Mumford et al., 1987).

The PAH and their analogues and derivatives are ubiquitous in the atmosphere. They are generally produced by combustion of carbonaceous fuels and by industrial processes. Major sources of PAH in outdoor air include combustion of gasoline and diesel fuels for transportation and combustion of oil, wood and coal for space heating and power production. Agricultural burning and forest fires can also be significant sources. The industrial processes that are sources of PAH in outdoor air include coke production, petroleum refining, and steel production. In homes and non-industrial buildings, the major sources are expected to be infiltration of outdoor air and indoor combustion sources such as cigarettes, unvented space-heaters, gas stoves, wood stoves, and fireplaces.

Depending upon their equilibrium vapor

pressures and the temperature of the environment, PAH are found in the gas phase, distributed between gas and particle phases, or entirely in the particle phase (Cautreels and Van Cauwenberghe, 1978; Ligocki and Pankow, 1989). Because PAH are generally produced by combustion, they are found in the respirable particle (D_{50} = 3.5 μm) fraction (Miguel and Friedlander, 1978; Van Vaeck and Van Cauwenberghe, 1985).

The California Health and Safety Code Section 39660.5 et seq., effective January 1987, requires the California Air Resources Board (CARB) to consider indoor exposures in assessing the risks to public health posed by toxic air contaminants. The PAH are among the classes of compounds about which there is concern. Measurements of outdoor concentrations of PAH have been made in California with sampling and analytical techniques that require the collection of large volumes of air using a high-volume sampler (Atkinson et al., 1988; Arey et al., 1989; Zielinska et al., 1989). Such methods are generally inappropriate for use indoors since the high sampling flow rates and volumes can cause substantial changes in ventilation rates and can reduce indoor concentrations of the contaminants.

The objectives of this study, sponsored by the CARB, were to: 1) develop a sampling system and analytical methods that are appropriate for measuring concentrations of selected gas- and particulate-phase PAH in indoor environments; 2) conduct a pilot field study in residences and commercial office

Table 1 Building and source characteristics for residential and commercial tests

Site ID†	Building Type	Floor Area/ Air Volume m^2 / m^3	Wood Stove kg burned		ETS No. cigs smoked		Gas Stove m^3 burned		Air Exchange Rate (1/h)	
			Day	Night	Day	Night	Day	Night	Day	Night
R-1	Detached Single-family Residence	110/ 254	–	–	–	–	–	–	0.14	0.30
R-2	Detached Single-family Residence	110/ 254	–	–	–	–	0.19	–	0.34	0.38
M-1	Detached Single-family Residence	144/ 332	–	–	14	1	–	–	0.34	0.47
T-1	Detached Single-family Residence	84/ 209	10.6	7.0	–	–	–	–	0.26	0.32
T-2	Detached Single-family Residence	84/ 209	6.4	2.8	11	4	0.14	–	0.23	0.31
S-1	Commercial Office Space 1-Floor zone	1280/ 6362*	–	–	–	–	–	–	0.96	
P-1	Commercial Office Space 6-Floor zone	5165/ 16,656**	–	–	22	–	–	–	0.80	

† T = Truckee; S = Sacramento; P = Palo Alto; R = Rodeo; M = Milbrae; 1 = Day/Night 1; 2 = Day/Night 2.
* The First floor has a separate ventilation system and was considered separately in calculating floor area and air volume.
** All six floors share the same ventilation system and were added together in calculating floor area and air volume.

spaces to validate the use of this sampler and these analytical methods; and 3) characterize the emissions of PAH in these environments from combustion processes which are indoor sources of PAH. The results of the entire study are presented in detail in the project report (Offermann et al., 1990). The results of the pilot field study are presented here.

Experimental

Study Design and Site Selection

For the field study, three single-family residences and two commercial office buildings, with and without three known indoor sources of PAH, were selected on a voluntary, non-random basis. All of the buildings are located in California (Table 1). Tests were conducted in these buildings to provide information on the precision and bias of the sampling and analytical methods under a variety of realistic indoor environmental conditions. Environmental tobacco smoke (ETS), gas cooking ranges, and wood stoves were selected as the indoor sources as they are possibly the most significant indoor sources of combustion-generated PAH. The activity of these sources was controlled by the investigators in order to be assured of emissions of PAH during the days of the tests. Five tests were conducted in the three residences, including: one test without active sources; one test with each of the three selected sources active; and one test with all three sources active. Tests were also conducted in two office buildings. One was a no-smoking building without active combustion sources. In the other building, without a smoking policy, cigarettes were smoked in an office suite at a controlled rate.

PAH Sampler

The sampling system is described in detail by Loiselle et al. (1991). The sampler is designed to collect a 25-m³ volume of air at a constant sampling rate of 34 l/min over a 12-h sampling period. The 12-h period allows comparisons of daytime and nighttime concentrations of PAH. The 25-m³ sample volume is the minimum necessary to achieve the desired detection limits for PAH of 0.01-1 ng/m³. The 34 l/min sampling rate is estimated to cause less than a 5% reduction in the indoor contaminant concentrations in typical residences. The sampler pump is a rotary-vane vacuum pump in an acoustically shielded fan-cooled enclosure. The noise criteria rating at a 1-m radius from the enclosure is NC-45. Non-compensating flow control is achieved with a manual valve. The sample airflow rate is measured with a calibrated rotameter. Operating time is recorded by an electro-mechanical timer. The pump draws air through a 47-mm Teflon-impregnated glass-fiber (TIGF) filter for the collection of particulate-phase PAH. The filter is followed by a section of 2.5-cm O.D. glass tubing containing cleaned XAD-4 resin in front and back sections (2.5 g each) for the collection of gas-phase PAH.

Field Measurements

In each residential test, samples for indoor and outdoor PAH were simultaneously collected over consecutive daytime (7 am to 7 pm) and nighttime 12-h sampling periods (7 pm to 7 am). Samplers were placed at a single location in the residence and at a single outdoor location adjacent to the building. The indoor samplers were placed near the center of the living/dining room area for both the daytime and nighttime measurements since this location has been demonstrated, in a survey of room-to-room concentrations of respirable particles, to provide a good measure of the average indoor concentration (Ju and Spengler, 1981). Duplicate side-by-side (collocated) samplers were deployed indoors at each residence during the daytime sampling period and outdoors at one residence during both the daytime and nighttime sampling periods.

In each of the office-building tests, samples for indoor and outdoor PAH were sim-

ultaneously collected over a single daytime (7 am to 7 pm) sampling period. Duplicate samplers were placed at a central location in an office suite and a single sampler was sited adjacent to the air inlet for the building.

The air flow rate through each sampler, corrected for standard temperature (25°C) and pressure (760 mm Hg) was measured every 2-3 h, and the pump was manually adjusted to re-establish the initial air flow rate as required. The 12-h, time-weighted average flow rate was computed by averaging the periodic measurements.

For each test, an air-exchange rate was measured concurrently with the collection of the simultaneous indoor and outdoor samples. This measurement was made at a location adjacent to the indoor samplers using a tracer-gas decay technique employing sulfur hexafluoride. The local age of air and the local ventilation rate at the sampling location were then computed (Offermann, 1988). The local ventilation rate may differ from the nominal building ventilation rate depending on the flow pattern of outside air to the measured zone.

The usage of the sources during the sampling periods was recorded in a detailed log. A dry-test meter was installed to measure the amount of gas consumption by the kitchen gas range in the tests with this appliance.

The additional data that were collected during each field test included: the number of occupants in the building and their smoking habits; any nearby outdoor sources of PAH (e.g., highways, airports, power plants); the number of floors, the floor area and the volume of air space in the building; the heating, ventilating, and air-conditioning characteristics of the building; the indoor and outdoor temperatures; the indoor relative humidity; and the local wind speed and direction.

A total of 42 samples for gas- and particulate-phase PAH were collected. These included 26 indoor samples and 11 pairs of collocated samples. A total of seven sample blanks were carried into the field and submitted for analysis.

Total Suspended Particles (TSP)

The total masses of particulate matter collected in the samples were computed from mass measurements of the filters before and after their use in the field. These mass measurements were made with electronic microbalance maintained at near 50% relative humidity. Since the filters were used without a size-selective inlet, the concentrations represent total suspended particulate (TSP) concentrations.

Analysis of Gas-Phase PAH

The analytical methods are described by Hodgson et al. (1990). The XAD-4 resin was cleaned by Soxhlet extractions with methanol and dichloromethane and dried to remove residual solvent. After packing a sorbent cartridge, the front section was spiked with three perdeuterated compounds (naphthalene-d_8, phenanthrene-d_{10} and pyrene-d_{10}) which served as surrogates for the determination of analyte recoveries. For analysis, the front and back section of resin from each sampler were separately extracted by sonication with dichloromethane. The extract of each section was filtered. The filtrate was solvent-exchanged to benzene and concentrated to 500 μl by rotary evaporation. The sample extracts were analyzed by electron impact, capillary gas chromatography-mass spectrometry. The molecular ions of the PAH were selectively monitored. Two separate analyses were performed. The 500-μl extracts of the front and back sections of each sampler were analyzed for compounds more volatile than phenanthrene. An internal standard for quantitation (n-dodecane-d_{26}) was added to these extracts. The extract of the front section was further concentrated to ~50 μl by blowdown and analyzed for the less-volatile compounds. Anthracene-d_{10} was added as the internal standard prior to this analysis.

Analysis of Particulate-Phase PAH

The analytical methods are described by Gundel et al. (1990). Half of each TIGF filter was extracted by sonication into a benzene-methanol (50/50, v/v) mixture. Fluoranthene-d_{10} was added as an internal standard for recovery. Extracts were filtered and concentrated to 500 μl in a rotary evaporator. Benzo(e)pyrene-d_{12} was added as an internal standard for quantitation. Analysis was by reverse-phase high-performance liquid chromatography (HPLC) with fluorescence detection. In order to determine closely-eluting and co-eluting pairs of PAH, each sample was analyzed under two different programmed sets of excitation and emission wavelengths.

Results

Building and Source Parameters

Table 1 summarizes pertinent building and source data for the field tests. All of the residences had forced-air gas heating systems. The gas furnace and water heater exhaust vents were inspected for leaks and were found to be in good condition. For the tests where a wood stove was used for heat, the gas furnace was not used. The local air exchange rates in the residences were slightly elevated at night relative to during the day. The primary source activity occurred during the daytime sampling periods. At night, a gas range was not used; only 1-4 cigarettes were smoked; and the amount of wood burned was less. The number of cigarettes in the office building represents the number smoked in the office suite in which the measurements were made. Both cigarette and pipe smoking occurred in adjacent offices.

TSP Measurements

Despite the relatively high loading of particulate matter on some filters (up to 6 mg) the air sampling rates for each sampler were found to remain very stable throughout the 12-h sampling period. The maximum manual adjustment to the air flow rate over 12 h was less than 7%, despite the fact that the air sampler had no automatic compensation for increases in the pressure drop across the filter.

The concentrations of TSP measured in indoor and outdoor air during the daytime and nighttime sampling periods are shown in Figure 1 for all of the tests. The highest indoor concentrations (120-260 μg/m³) occurred in the tests with a high rate of smoking and/or with an active wood stove. The outdoor concentrations of TSP ranged from 10-64 μg/m³.

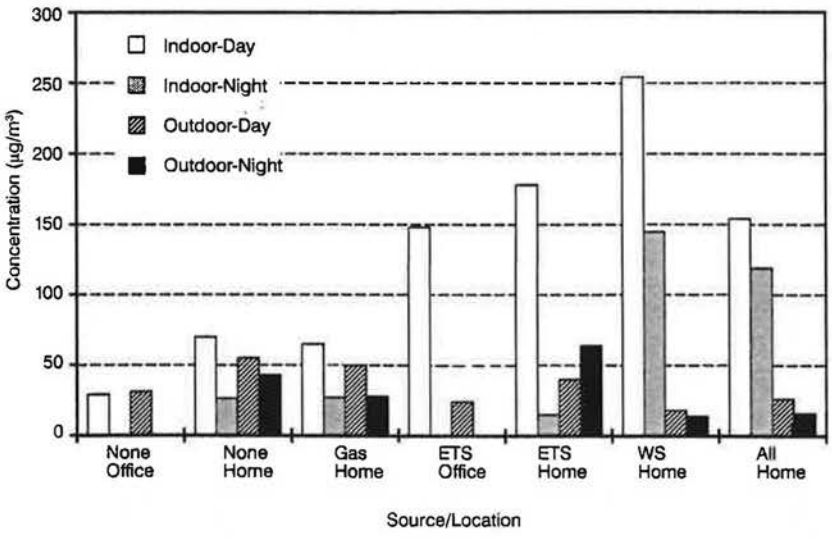

Fig. 1 Indoor and outdoor concentrations of total suspended particles by source and building type. None = no unvented combustion; gas = gas range; ETS = environmental tobacco smoke; WS = wood stove; all = gas + ETS + WS.

Table 2 Precisions of concentrations of gas-phase PAH determined from pairs of collocated samples

	Indoor + Outdoor				Indoor				Outdoor			
	n	Mean† (ng/m^3)	Abs* Prec. (ng/m^3)	Rel.** Prec. (%)	n	Mean† (ng/m^3)	Abs* Prec. (ng/m^3)	Rel.** Prec. (%)	n	Mean† (ng/m^3)	Abs* Prec. (ng/m^3)	Rel.** Prec. (%)
Naphthalene	11	1160	160	14	7	1680	215	13	4	254	15	6
2-Methylnaphthalene	11	524	47	9	7	743	63	9	4	141	14	10
1-Methylnaphthalene	11	277	26	9	7	399	35	9	4	63	6.2	10
Biphenyl	11	338	120	36	7	447	151	34	4	147	92	62
Acenaphthylene	11	56	2.7	5	7	82	3.6	4	4	10	0.9	9
Acenaphthene	11	14	3.6	25	7	20	4.8	24	4	4.6	0.9	20
Fluorene	11	27	3.6	13	7	39	4.8	12	4	7.2	1.2	16
Phenanthrene	11	45	51	113	7	61	69	114	4	18	2.9	16
Anthracene	11	12	10	80	7	18	13	71	4	1.2	0.2	19
2-Methylanthracene	9	1.5	0.3	22	7	1.8	0.4	21	<3			
9-Methylanthracene	3	0.5	0.8	160	3	0.5	0.8	160	<3			
Fluoranthene	11	6.8	1.2	17	7	6.8	0.6	9	4	6.9	2.2	33
Pyrene	11	6.2	0.6	10	7	7.3	0.6	8	4	4.2	0.9	22
Chrysene	8	0.8	0.2	22	6	0.9	0.2	21	<3			

† Mean concentration for n sample pairs calculated for pairs ($n \geq 3$) with concentrations above detection limits.
* Absolute precision reported as the 95% confidence interval computed from the pooled variance for n sample pairs.
** Relative precision computed as the absolute precision divided by the mean concentration for n sample pairs.

Gas-Phase PAH Measurements

The sorbent-cartridge samples and field blanks were analyzed for 14 PAH ranging in volatility from naphthalene through chrysene. These compounds are listed in Table 2. The recoveries of the three surrogate compounds for the field blanks and the outdoor samples averaged 70-80% with 95% confidence intervals of ~20%. Some of the indoor samples had low apparent recoveries of phenanthrene-d_{10} and high apparent recoveries of pyrene-d_{10}. This was attributed to the presence of a contaminant in these samples which interfered with the analysis of phenanthrene-d_{10} and with anthracene-d_{10}, the internal standard. The source of this contaminant has not yet been identified. The effect of the contaminant was largely mitigated by the use of pyrene-d_{10} as the internal standard for these samples. Naphthalene and biphenyl exhibited a small percentage breakthrough from the front to the back sorbent section in some samples. The sample values are corrected for incomplete recovery and any breakthrough. Six of the 14 compounds analyzed had measurable sorbent blanks. These blanks were generally less than 2% of their respective median masses in the samples. The lower limit of detection for compounds with no measurable blank values was estimated to be near 0.06 ng/m^3. These are reported as 0.1 ng/m^3 in the Tables.

The overall precision of the method for gas-phase PAH was computed from the data generated by the 11 pairs of indoor and outdoor collocated samples (7 indoor and 4 outdoor pairs). The pooled variance was computed for each compound according to standard analysis of variance techniques (Ku et al., 1969). Then, a 95% confidence interval in ng/m^3 was computed by multiplying the pooled standard deviation by the value of the Student's t distribution for n degrees of freedom, where the degrees of freedom equal the number of sample pairs. Relative precisions were computed by dividing the 95% confidence intervals by the mean values for each pool of paired samples. If the concentrations for a compound were below the method detection limit for one or both of the samples

in a pair, the data for this pair were excluded from the precision analysis.

The results of these computations for the gas-phase PAH are presented in Table 2 for the combination of indoor and outdoor sample pairs and separately for the indoor and outdoor sample pairs. The relative precision of the gas-phase PAH for the combined indoor and outdoor samples ranged from 5% for acenaphthylene to 160% for 9-methylanthracene. The high relative imprecision for 9-methylanthracene was largely the result of concentrations that were at or near the detection limit. The other compounds with relative precisions in excess of 25% for combined indoor and outdoor samples were biphenyl, phenanthrene, and anthracene.

By examining the relative precisions of the indoor and outdoor concentrations separately, it is apparent that the high relative imprecisions for phenanthrene and anthracene in the combined indoor and outdoor samples were a result of the high relative imprecisions of the indoor samples. As discussed above, there was a contaminant present in some indoor samples which compromised the measurement precisions of these two compounds. The high relative imprecision for biphenyl is unexplained.

In a separate analysis, uncertainty pertur-

Table 3 Twelve-hour, time-weighted average concentrations of gas-phase PAH by location and source category

Building and Source†	Location-Time	Concentration (ng/m³)*													
		NAPH	2NAPH	1NAPH	BiPHE	ACNPY	ACNPE	FLRN	PHEN	ANTH	2ANTH	9ANTH	FLUOR	PYREN	CHRYS
Residential	In-Day	**1290**	**925**	**463**	**373**	**16.5**	**17.1**	**44.9**	**109**	**9.6**	**0.9**	**<0.1**	**4.1**	**3.1**	**0.1**
R-1	In-Night	**1270**	**919**	**464**	**263**	**14.2**	**14.4**	**39.6**	**51.0**	**2.6**	**0.5**	**<0.1**	**3.0**	**2.2**	**<0.1**
None	Out-Day	469	216	98	378	6.4	6.2	11.0	21.6	0.6	0.1	<0.1	4.1	2.7	0.2
	Out-Night	367	158	68	135	4.1	2.7	4.6	9.6	0.1	<0.1	<0.1	1.6	1.3	<0.1
Residential	In-Day	**1150**	**841**	**420**	**421**	**15.1**	**11.9**	**38.6**	**37.2**	**2.6**	**0.6**	**<0.1**	**2.6**	**2.0**	**0.2**
R-2	In-Night	**1060**	**846**	**426**	**332**	**13.1**	**12.7**	**38.8**	**38.1**	**2.0**	**5.7**	**<0.1**	**2.7**	**1.9**	**0.1**
Gas	Out-Day	283	124	54	94	4.6	2.6	4.4	6.0	0.3	<0.1	<0.1	1.5	1.3	<0.1
Residential	In-Day	**3300**	**534**	**312**	**497**	**29.1**	**13.0**	**28.3**	**102**	**11.7**	**2.2**	**0.1**	**4.0**	**3.1**	**0.9**
M-1	In-Night	**1690**	**390**	**217**	**425**	**19.9**	**11.9**	**22.2**	**51.2**	**4.6**	**1.8**	**0.1**	**3.5**	**2.9**	**0.6**
ETS	Out-Day	741	258	128	639	7.4	5.2	14.3	17.9	0.5	0.2	<0.1	4.1	2.5	0.3
	Out-Night	727	276	122	206	9.1	6.1	7.8	9.8	0.4	0.1	<0.1	1.4	0.9	<0.1
Residential	In-Day	**1710**	**1100**	**567**	**516**	**62.3**	**24.4**	**41.9**	**37.7**	**23.3**	**1.2**	**0.1**	**4.3**	**4.9**	**0.4**
T-1	In-Night	**1830**	**991**	**507**	**421**	**54.2**	**35.5**	**41.0**	**34.2**	**18.5**	**0.9**	**<0.1**	**4.0**	**4.8**	**0.4**
Wood	Out-Day	307	167	75	64	19.3	4.8	7.8	17.6	2.0	0.5	<0.1	3.0	2.9	0.2
	Out-Night	119	56	28	70	7.5	8.7	10.5	19.4	1.8	0.2	<0.1	2.6	2.1	<0.1
Residential	In-Day	**2870**	**877**	**530**	**572**	**406**	**43.8**	**63.1**	**68.0**	**45.8**	**2.3**	**0.6**	**19.6**	**29.4**	**2.1**
T-2	In-Night	**2030**	**834**	**463**	**395**	**151**	**28.6**	**37.9**	**81.5**	**8.9**	**1.5**	**<0.1**	**5.5**	**6.9**	**0.6**
All	Out-Day	297	143	67	112	9.6	29.4	31.3	51.0	6.1	0.4	<0.1	4.9	3.2	0.2
	Out-Night	232	120	57	94	7.9	24.0	28.2	51.7	5.8	0.7	0.2	5.2	3.4	0.3
Commercial	In-Day	**511**	**311**	**142**	**449**	**6.7**	**11.1**	**23.7**	**43.3**	**1.2**	**0.2**	**<0.1**	**6.3**	**3.4**	**0.2**
S-1, **None**	Out-Day	340	211	92	393	5.6	3.8	7.2	31.2	0.5	<0.1	<0.1	20.5	10.4	0.6
Commercial	In-Day	**926**	**614**	**365**	**306**	**38.9**	**16.6**	**30.9**	**28.2**	**33.8**	**5.4**	**0.8**	**7.0**	**5.5**	**1.8**
P-1, **ETS**	Out-Day	252	132	58	62	7.0	1.3	3.4	5.3	0.5	<0.1	<0.1	1.3	1.4	<0.1

† **None** = no unvented combustion, **Gas** = Gas stove, **ETS** = environmental tobacco, **Wood** = wood stove, **All** = Gas + ets + wood.

* NAPH = Naphthalene, 2NAPH = 2-Methylnaphthalene, 1NAPH = 1-Methylnaphthalene, BiPHE = Biphenyl, ACNPY = Acenaphthylene, ACNPE = Acenaphthalene, FLRN = Fluorene, PHEN = Phenanthrene, ANTH = Anthracene, 2ANTH = 2-Methylanthracene, 9ANTH = 9-Methylanthracene, FLUOR = Fluoranthene, CHRYS = Chrysene.

Table 4 Precisions of concentrations of particulate-phase PAH determined from pairs of collocated samples

	Indoor + Outdoor				Indoor				Outdoor			
Compound	n	Mean† (ng/m³)	Abs* Prec. (ng/m³)	Rel.** Prec. (%)	n	Mean† (ng/m³)	Abs* Prec. (ng/m³)	Rel.** Prec. (%)	n	Mean† (ng/m³)	Abs* Prec. (ng/m³)	Rel.** Prec. (%)
Fluoranthene[a]	7	0.4	1.2	340	4	0.5	1.9	347	3	0.1	0.3	283
Pyrene[a]	4	5.4	6.3	118	4	5.4	6.3	118	<3			
Benzo(a)anthracene	5	0.3	0.2	68	3	0.4	0.3	69	<3			
Chrysene[a]	8	2.2	5.6	251	4	4.3	7.6	178	4	0.2	0.4	181
Benzo(e)pyrene	4	1.5	1.0	66	4	1.5	1.0	66	<3			
Benzo(b)fluoranthene	8	0.5	0.1	25	4	0.8	0.2	21	4	0.2	0.1	62
Benzo(k)fluoranthene	11	0.1	0.04	30	7	0.2	0.05	29	4	0.1	0.04	46
Dibenzo(a,c)anthracene[b]	4	0.3	1.2	421	4	0.3	1.2	421	<3			
Benzo(a)pyrene	10	0.8	1.5	178	6	1.2	2.2	172	4	0.2	0.2	89
Benzo(g,h,i)perylene	11	1.1	1.1	100	7	1.5	1.4	94	4	0.3	0.4	144
Indeno(1,2,3-cd)pyrene	11	0.6	0.3	43	7	1.8	0.3	42	4	0.3	0.2	62
Coronene[c]	8	0.8	1.1	126	5	0.1	1.4	132	3	0.5	0.9	175

Phenanthrene, anthracene, 5-methylchrysene, retene, dibenzo(a,l)pyrene, dibenzo(a,h)pyrene, dibenzo(a,e)pyrene, dibenzo(a,i)pyrene, and dibenzo(a,h)pyrene had < 3 sample pairs with concentrations above detection limits and were omitted.

† Mean concentration for n sample pairs calculated for pairs ($n \geq 3$) with concentrations above detection limits.

* Absolute precision reported as the 95% confidence interval computed from the pooled variance for n sample pairs.

** Relative precision computed as the absolute precision divided by the mean concentrations for n sample pairs.

[a] Interference observed when ETS or wood smoke was present.

[b] Detected only when ETS or wood smoke was present.

[c] Interference observed in many indoor and outdoor samples.

bation theory was used to compute the theoretical measurement precisions for the concentrations from the sum of the estimated uncertainties introduced by each of the input variables. Such an analysis is useful to examine the impacts of each measurement variable upon the precision of the method.

The precision of the method for the concentrations of the gas-phase PAH was determined from the uncertainties in the volumes of air sampled and the masses of the PAH in the sample. The uncertainty in the air-volumes was estimated to be 2%, and the typical uncertainty in the analysis of the mass of a compound was near 20%. These estimates were combined as the square root of the sum of the squares of the individual uncertainties to yield the total uncertainty for concentration. The calculated uncertainty of 21% is nearly equal to the uncertainty in the analysis of mass. There is reasonable agreement between the total uncertainty calculated in this manner and the measured uncertainties presented in Table 2, with the exception of four compounds.

The 12-h, time-weighted average concentrations of the 14 gas-phase PAH measured in the field study are summarized in Table 3. Values for the collocated sample pairs have been averaged. Values below the stated detection limit were averaged as one-half of the detection limit.

Particulate-Phase PAH Measurements

The filters and field blanks were analyzed for 21 PAH. Lower limits of detection were individually calculated for the compounds as three times the standard deviation of their values for the field blanks. Those 12 PAH, for which at least 3 pairs of samples had concentrations above the detection limits, are listed in Table 4 in order of increasing retention time. Fluoranthene through chrysene are semi-volatile compounds, i.e., they partition between gas and particle phases. Benzo(e)pyrene and longer-retained compounds

Table 5 Twelve-hour, time-weighted average concentrations of particulate-phase PAH by location and source category

Building and Source†	Location-Time	Concentration (ng/m³)*											
		Fluor	Pyren	BaA	Chrys	BeP	BbF	BkF	BaP	DBahA	BghiP	IcdP	Coron
Residential	In-Day	**<.04**	**<.11**	**<.04**	**<.03**	**<.21**	**0.042**	**0.01**	**0.038**	**<.11**	**0.16**	**0.14**	**0.33**
R-1	In-Night	**<.04**	**<.14**	**<.04**	**0.08**	**<.21**	**0.079**	**0.02**	**<.018**	**<.11**	**0.25**	**0.24**	**int**
None	Out-Day	0.06	<.11	0.07	0.07	<.21	0.10	0.04	0.12	<.11	0.24	0.16	0.45
	Out-Night	<.04	<.11	0.09	0.15	<.21	0.26	0.06	0.069	<.11	0.44	0.22	int
Residential	In-Day	**0.05**	**<.11**	**<.04**	**<.03**	**<.21**	**0.053**	**0.02**	**0.036**	**<.11**	**0.13**	**0.14**	**int**
R-2	In-Night	**<.04**	**0.20**	**0.12**	**int**	**<.21**	**<.042**	**<.01**	**<.018**	**<.11**	**<.07**	**<.04**	**<.01**
Gas	Out-Day	0.07	<.11	0.05	0.08	<.21	0.14	0.05	0.077	0.12	0.26	0.27	int
	Out-Night	<.04	<.11	<.04	0.14	<.21	0.088	0.01	0.022	<.11	<.07	<.04	<.01
Residential	In-Day	**0.86**	**1.6**	**0.13**	**0.62**	**int**	**0.42**	**0.13**	**0.60**	**0.18**	**0.88**	**0.55**	**0.54**
M-1	In-Night	**0.07**	**0.19**	**<.04**	**0.30**	**0.58**	**0.25**	**0.05**	**0.20**	**0.29**	**0.57**	**0.30**	**<.01**
ETS	Out-Night	0.12	<.11	0.06	0.04	0.19	0.097	0.04	0.094	<.11	0.28	0.20	0.29
	Out-Night	0.05	<.11	<.04	0.11	0.16	0.099	0.21	0.045	<.11	0.55	0.25	<.01
Residential	In-Day	**0.13**	**int**	**0.20**	**2.4**	**2.1**	**0.23**	**0.07**	**0.13**	**<.11**	**0.19**	**0.12**	**0.11**
T-1	In-Night	**<.04**	**int**	**<.04**	**2.5**	**int**	**0.047**	**0.02**	**0.045**	**0.22**	**0.32**	**0.07**	**<.01**
Wood	Out-Day	0.06	0.12	0.21	0.22	0.33	0.35	0.15	0.37	<.11	0.59	0.36	0.83
	Out-Night	0.22	int	0.10	0.22	<.21	0.26	0.12	0.19	<.11	0.20	0.25	0.20
Residential	In-Day	**2.0**	**int**	**0.61**	**int**	**2.4**	**2.1**	**0.74**	**6.6**	**2.6**	**8.8**	**4.1**	**4.0**
T-2	In-Night	**0.06**	**int**	**0.05**	**0.17**	**0.37**	**0.19**	**0.06**	**0.20**	**<.11**	**0.11**	**0.35**	**<.01**
All	Out-Day	0.18	<.11	0.16	0.14	0.60	0.22	0.10	0.23	<.11	0.22	0.31	<.01
	Out-Night	<.04	0.13	<.04	0.56	<.21	0.22	0.06	0.14	<.11	0.16	0.21	<.01
Commercial	In-Day	**0.07**	**<.11**	**<.04**	**0.06**	**<.21**	**0.16**	**0.04**	**0.044**	**<.11**	**0.18**	**0.16**	**0.09**
S-1, None	Out-Day	0.07	0.13	<.04	0.28	<.21	0.18	0.04	0.12	<.11	0.17	0.22	0.45
Commercial	In-Day	**0.22**	**0.82**	**0.52**	**int**	**0.39**	**0.58**	**0.15**	**0.38**	**<.11**	**0.44**	**0.50**	**<.01**
P-1, ETS	Out-Day	<.04	<.11	<.04	0.09	<.21	0.098	0.02	0.030	<.11	0.22	0.19	int

† **None** = no unvented combustion, **Gas** = Gas stove, **ETS** = environmental tobacco smoke, **Wood** = wood stove, **All** = Gas + ets + wood.

* Fluor = Fluoranthene, Pyren = Pyrene, BaA = Benzo(a)anthracene, Chrys = Chrysene, BeP = Benzo(e)pyrene, BbF = Benzo(b)fluoranthene, BkF = Benzo(k)fluoranthene, BaP = Benzo(a)pyrene, DBahA = Dibenzo(a,h)anthracene, BghiP = Benxo(g,h,i)perylene, IcdP = Indeno(c,d)pyrene, Coron = Coronene. **Int.** = interference.

(five-rings and larger) are non-volatile compounds found primarily in the particle phase (Cautreels and Van Cauwenberghe, 1978; Ligocki and Pankow, 1989).

Means and standard deviations for recoveries of fluoranthene-d_{10} were 81 ± 11% and 68 ± 18% for blanks and field samples, respectively. The sample PAH values were not corrected for recovery of fluoranthene-d_{10} because it was not known at the time of data analysis whether losses of this semi-volatile compound accurately reflected losses of the less volatile PAH. Subsequent work with standard reference material SRM-1649, urban air particulate matter, has found that losses of fluoranthene-d_{10} do indeed scale with losses of the whole range of particulate-phase PAH (L.A. Gundel, unpublished data).

The precision of the method for particulate-phase PAH was computed in the same way as for the gas-phase PAH (Table 4). When the indoor and outdoor sample pairs were considered together, the relative precisions were dominated by any observed large differences between sample pairs from indoor locations with cigarette and/or wood smoke. The relative precisions for outdoor and indoor samples were similar, but the absolute precisions for the outdoor samples were substantially lower for all PAH for which there were sufficient data for comparison. Six PAH could be determined with rela-

tive precisions of 100% or less: benzo(a)anthracene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene and indeno(c,d)pyrene. Precisions for all compounds have subsequently been improved by correcting for the loss of fluoranthene-d_{10}.

As discussed by Gundel et al. (1990), samples with cigarette and wood smoke had two recurrent difficulties: interfering compounds and a high fluorescence background. High imprecision was found for any PAH for which unidentified interference(s) hindered quantitation. The presence of interferences was indicated by large differences between samples and standards in fluorescence ratios at two sets of fluorescence conditions. Interferences were especially troublesome for the semi-volatile compounds: phenanthrene, anthracene, fluoranthene, pyrene and chrysene. The relative precisions for these compounds ranged from 118-340%. Subsequent work has found that the semi-volatile PAH from these sources can be determined by HPLC when the sample extracts are cleaned up before analysis (L.A. Gundel, unpublished data). In indoor samples with cigarette or wood smoke, benzo(a)pyrene had high mean concentrations and relatively large differences between sample pairs. Interferences were also sometimes observed for several less volatile compounds in both indoor and outdoor samples. No explanation has been found for the high imprecision in the determination of dibenzo(a,c)anthracene.

The 12-h, time-weighted average concentrations of 12 selected particulate-phase PAH are presented in Table 5. The complete data set for all 21 compounds is found in Offermann et al. (1990). Interferences indicated by fluorescence ratios are noted in the table.

Discussion

Very few measurements of indoor concentrations of PAH have been reported. Wilson and Chuang (1991) compared concentrations of PAH and indicators of tobacco smoking in two houses, one with smokers and the other without smokers. Mumford et al. (1990) reported concentrations of PAH in a mobile home, with and without the operation of an unvented kerosene heater. An elevation in the concentrations of some of the particulate-phase PAH was observed when the heater was in use. Wilson et al. (1989) presented concentration data for an office without active combustion sources. Wilson et al. (1990) summarized data on PAH concentrations for five California homes and for small numbers of homes in three other studies. They found that indoor concentrations generally exceeded outdoor concentrations. Tobacco smoking was identified as a major source, typically resulting in an increase by a factor of three to four in overall PAH concentrations in homes with smokers compared to homes without smokers. The other identified indoor residential sources were wood smoke, natural gas appliances and vehicle exhaust. Daisey et al. (1989) compared indoor concentrations of PAH in seven Wisconsin homes with and without a wood stove in operation. Concentrations were 2-46 times higher during periods of wood burning. Out-

Table 6 Comparison of indoor and outdoor concentrations of gas-phase PAH

Compound	Indoor Mean (ng/m³)	Outdoor Mean (ng/m³)	In/Out Ratio	Sig. Diff.*
Naphthalene	1700	437	3.9	+
2-Methylnaphthalene	762	214	3.6	+
1-Methylnaphthalene	407	105	3.9	+
Biphenyl	425	223	1.9	+
Acenaphthylene	74.3	11.0	6.8	+
Acenaphthene	20.9	10.1	2.1	+
Fluorene	38.1	14.4	2.6	+
Phenanthrene	51.5	24.1	2.1	+
Anthracene	14.1	4.9	2.9	+
2-Methylanthracene	1.6	0.7	2.3	+
Fluoranthene	5.8	5.2	1.1	
Pyrene	6.2	3.4	1.8	+
Chrysene	0.6	0.3	2.0	

*+= Significant median difference at 95% confidence level.

door concentrations were not measured so it is not clear if the elevated concentrations were due to indoor emissions from the stoves or infiltration of outdoor air contaminated with wood smoke. It is difficult to compare any of these results with the results of this study because the parameters which determine indoor concentrations (i.e., outdoor concentrations, indoor source activities, building ventilation rates and building air volumes) were generally not measured or reported.

Indoor and outdoor concentrations of gas-phase PAH were compared for the 11 sets of samples simultaneously collected indoors and outdoors at each of the field sites (in residences during the 12-h daytime and nighttime sampling periods, and in office buildings during the 12-h daytime sampling period) using a non-parametric sign test (Table 6). The average indoor concentrations were significantly higher at the 95% confidence level than the outdoor concentrations for all of the 14 gas-phase PAH, except for fluoranthene, chrysene, and 9-methylanthracene (not shown since most values were below the detection limit). The average indoor/outdoor concentration ratios for these compounds ranged from 2-4 for most compounds.

Indoor and outdoor concentrations of particulate-phase PAH were also compared for the 11 sets of simultaneously collected samples using a non-parametric sign test. Only when concentrations of a compound were above the detection limit in six or more sets was the test performed for that compound. The indoor concentrations of anthracene, pyrene, benzo(e)pyrene, dibenzo(a,e)pyrene and coronene were significantly higher at the 95% confidence level than their respective outdoor concentrations. However, as noted above, the determination of these compounds was often subject to interference in samples containing cigarette and/or wood smoke.

Indoor/outdoor concentration ratios are compared in Figure 2 by source and building type for particulate-phase PAH which had relative precisions at or below 100% and were not subject to interference. Benzo(a)pyrene was included because of its importance as a carcinogen even though its indoor measurements were subject to high relative imprecision. These non-volatile compounds showed lower concentrations indoors than outdoors in the residential tests (ratio = 0.3-0.5) except when cigarette smoke was present (ratio = 3-40). In contrast to results for the gas-phase PAH, the non-volatile PAH had lower

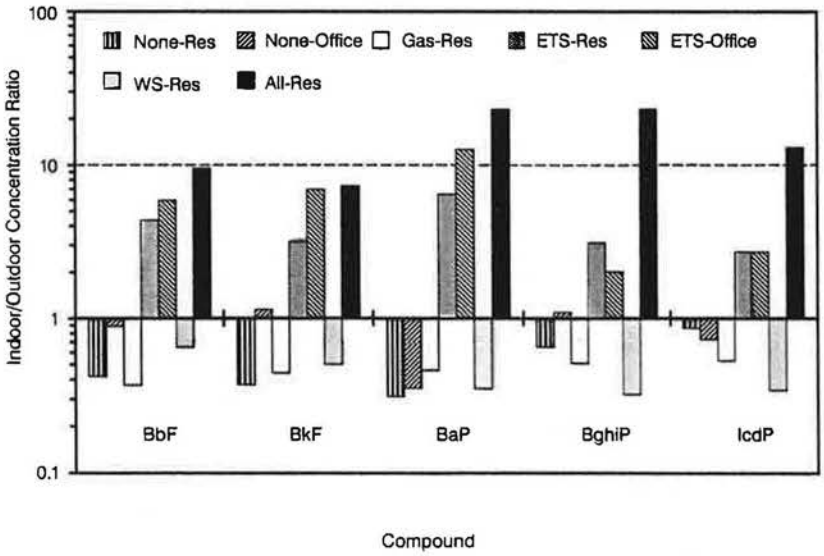

Fig. 2 Indoor/outdoor concentration ratios for selected particulate-phase PAH by source and building type. BbF = benzo(b)fluoranthene; BkF = benzo(k)fluoranthene; BaP = benzo(a)pyrene; BghiP = benzo(g,h,i)perylene; IcdP = indeno(c,d)pyrene.

concentrations indoors than outdoors when wood buring was the only indoor combustion source. Indoor/outdoor ratios of less than one have previously been reported for particulate-phase PAH in residences with wood smoke (Traynor et al., 1987). The office building where smoking occurred showed the same pattern as observed in the residences with cigarette smoke. Indoor/outdoor ratios were near one for the non-smoking office building, except for benzo(a)pyrene with a ratio of 0.35. These results suggest that the particulate-phase PAH have no appreciable net indoor sources except cigarette smoke.

This study was specifically designed to collect data on outdoor PAH concentrations, source activities, and local ventilation rates so that indoor net emission rates could be determined for all of the investigated sources. With this approach, it is then possible to quantify the impacts of these sources on indoor air quality in a way that allows comparisons among buildings and to estimate indoor concentrations of PAH in buildings with different ventilation rates, source activity patterns, or outdoor concentrations.

An indoor net emission rate is the combined rate of indoor source generation of a compound and its indoor removal. The net emission was computed using a simple steady-state, mass-balance model as the product of the local ventilation rate and the difference between simultaneously measured indoor and outdoor concentrations. A negative indoor net emission rate can occur if the indoor removal rate is greater than the indoor source generation rate. Indoor net emission rates of the gas-phase PAH were calculated for all of the residential and office building tests. In general, the residential emission rates of compounds less volatile than anthracene were mostly below the estimated minimum measurable net emission rate of 0.5 ng/m³-h. The lack of adequate precision for the particulate-phase PAH generally precluded the analysis of net indoor emission rates for these compounds.

With a few exceptions, the gas-phase PAH all had positive indoor net emission rates in the residential tests. These ranged from 870 ng/m³-h for the most volatile compound, naphthalene, to less than 1 ng/m³-h for the less volatile compounds (i.e., 2-methylanthracene through chrysene). The net emission rates of naphthalene through anthracene in the residential tests are plotted in Figure 3. The average of the daytime and nighttime emission rates are presented for residential test, R-1, without indoor unvented combustion sources. The daytime emission rates are

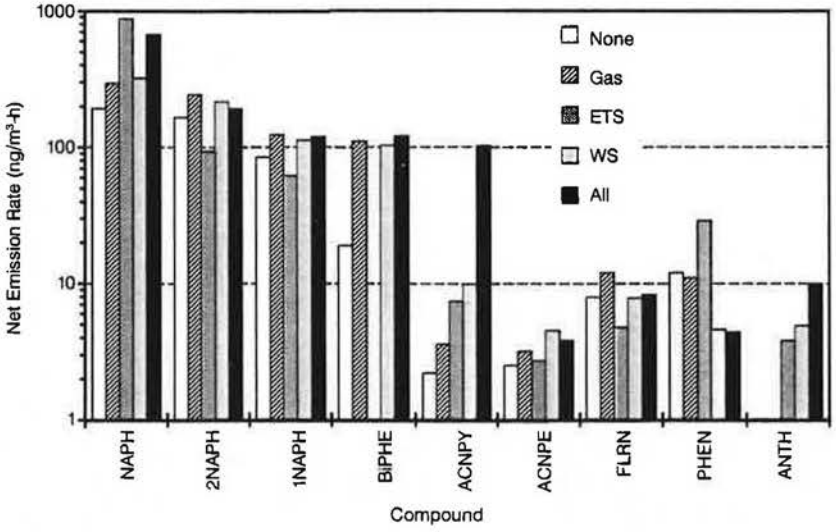

Fig. 3 Indoor net emission rates of selected gas-phase PAH for the residential tests. See Figure 1 and Table 3 for definitions of abbreviations.

presented for the other residential tests since the source activities were higher during the day (Table 1).

For the residential test without indoor unvented combustion sources, significant indoor net emission rates were indicated for all compounds shown in Figure 3, except anthracene. It is possible that there were noncombustion indoor sources of these compounds, such as various petroleum-based products, present in the house. Another possibility is that there were combustion sources previously active in the house which resulted in adsorption of the compounds onto surfaces with subsequent desorption occurring during the sampling periods when the sources were absent or inactive (Tichenor et al., 1991). Although not shown in Figure 3, there were differences in the net emission rates for naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, and fluorene between the daytime and nighttime sampling periods for this test, with the nighttime emission rates approximately double their respective daytime rates. The indoor and outdoor concentrations were nearly the same in both periods; however, the ventilation rate doubled. This suggests that the emission rates may have increased with the increased ventilation rate.

It is particularly interesting to compare the tests that were conducted in the same residence but with different sources since the emission rates due to any unidentified background sources and/or desorption from surfaces should be similar from day to day. The test without active sources and the test with only a gas cooking range were performed in this order on successive days in one house. From Figure 3, it appears that the gas range is a likely source of biphenyl and perhaps a minor source of all of the other compounds except phenanthrene and anthracene. The tests with the wood stove and with all of the sources active, including cigarette smoking, were also conducted on successive days in one house. The increases in the emission rates of naphthalene, acenaphthylene, and anthracene that were measured are probably attributable to the addition of environmental tobacco smoke (ETS) as a source.

There is more uncertainty when comparisons are made among emission rates measured in different buildings. Given this uncertainty, a comparison of the residential test with only cigarette smoking to the tests without active sources and with only a gas range active also suggests that ETS is a source of naphthalene, acenaphthylene, and anthracene. The indoor net emission rates of nine gas-phase PAH in the office buildings with and without tobacco smoking are presented in Figure 4. The emission rates of all of the compounds are higher in the building with ETS, with particularly noticeable differences for acenaphthylene and anthracene. Schmeltz et al. (1976) have shown that naphthalene and the methylnaphthalenes are present in cigarette smoke. When the residential test with wood smoke is compared in Figure 3 to the tests without active sources and only a gas range active, it appears that wood smoke may be a source of biphenyl, acenaphthylene, and anthracene.

In the office-building test without active combustion sources, there were substantial negative net emission rates for two of the less volatile gas-phase PAH not shown in Figure 4. Fluoranthene had an indicated emission rate of -14 ng/m³-h, and pyrene had an emission rate of -7 ng/m³-h. These negative rates suggest that these compounds are being removed by the HVAC air filters and adsorption onto indoor surfaces.

Net emission rates were calculated for the six particulate-phase PAH which showed relative precisions of 100% or better and for locations for which the estimated coefficient of variation for the emission rate was 65% or less. The emission rates for benzo(b)fluoranthene were 0.11 ± 0.07 and 0.4 ± 0.1 ng/m³-h for the residential tests with cigarette smoking (M-1) and all sources active (T-2), respectively. Emission rates for test T-2 for ben-

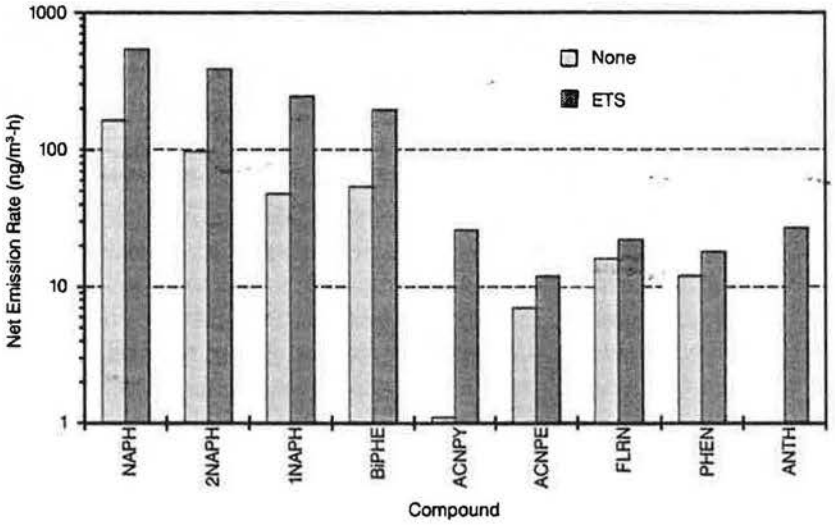

Fig. 4 Indoor net emission rates of selected gas-phase PAH in smoking and no-smoking office buildings. See Figure 1 and Table 3 for definitions of abbreviations.

zo(k)fluoranthene, benzo(a)pyrene, benzo-(ghi)perylene and indeno(c,d)pyrene were 0.15 ± 0.04, 1.5 ± 0.2, 2.0 ± 0.2 and 0.9 ± 0.4 ng/m³-h, respectively. These values are one to two orders of magnitude lower than the emission rates for the gas-phase PAH (Figures 3 and 4). Particulate retene, a marker for wood smoke, had an emission rate of 7 ± 2 ng/m³-h for the test with only this source.

Conclusions

The sampling and analytical method for gas-phase PAH developed for this study has several advantages over most previously reported methods. The relatively low sample volume of 25 m³ collected over 12 hours is well-suited for residences since indoor concentrations would typically be reduced by less than 5% as the result of sampling. The method utilizes only a relatively small amount of sorbent material (5 g of XAD-4) which reduces the potential for background contamination from the sorbent. Extraction of the sorbent using sonication is efficient and much simpler than Soxhlet extraction. In addition, sample cleanup procedures are not essential, even for samples collected in environments highly contaminated with ETS and wood smoke. This minimizes the sample processing steps and reduces the chances for loss of the analytes.

Despite the problems discussed above, the HPLC-based method for the analysis of the particulate-phase PAH shows considerable promise and can already be used for five- and six-membered ring PAH. Further developmental work is being undertaken as recommended by Gundel. Recently developed cleanup procedures for samples contaminated with cigarette and wood smoke have greatly reduced the interferences encountered in this study. Specificity has also been improved by using different programmed sets of excitation and emission wavelengths.

This study demonstrated the utility of a simple mass-balance model for evaluating *in situ* the magnitude of indoor combustion sources of PAH. Because ventilation rates and indoor and outdoor concentrations of PAH were simultaneously measured in conjunction with the use of the sources, it was possible to calculate net emission rates of PAH associated with these sources.

With few exceptions, the gas-phase PAH all had positive indoor net emission rates. In general, the most volatile gas-phase PAH had the highest net emission rates. In addition, the overall net emission rates for the gas-phase PAH were greater for those indoor en-

...surements with the most indoor unvented ...combustion activity (i.e., cigarette smoking ...and wood stove use). However, even in the ...residential and office building tests without ...active indoor combustion sources, many of ...the gas-phase PAH had substantial net emis... ...suggesting the presence of unidentified ...indoor sources.

The calculated net emission rates for the ...gas-phase PAH suggest that the use of gas ...ranges is probably a relatively minor source ...of gas-phase PAH except for biphenyl which ...was elevated in one of the residential tests ...with this appliance. Cigarette smoking and ...the use of a wood stove were more significant ...sources of gas-phase PAH as demonstrated ...by the observed increases in the net emission ...rates for tests with these sources. Environ...mental tobacco smoke was identified as a ...source of naphthalene, acenaphthylene, and ...anthracene, and wood smoke was identified ...as a likely source of biphenyl, acenaphthy...lene, and anthracene.

Environmental tobacco smoke was the ...only substantial source of the particulate-...phase PAH. The indoor concentrations of six ...non-volatile PAH (benzo(e)pyrene, ben...zo(b)fluoranthene, benzo(k)fluoranthene, ...benzo(a)pyrene, benzo(g,h,i)perylene, and in...deno(c,d)pyrene) were significantly elevated ...in tests with cigarette smoking. In environ...ments without active combustion sources, ...the indoor concentrations of these com...pounds were lower than their outdoor con...centrations.

Further studies of emission rates of PAH ...from various sources under controlled condi...tions in residences and office buildings using ...techniques similar to those employed in this ...study would be useful to increase our under...standing of the relative significance of these ...sources with respect to human exposures. ...Evaluation of multiple sources in single en...vironments, as was done for several of the ...tests presented here, should provide the best ...chance for determining significant differ...ences among the sources. Adsorption and de...sorption of PAH on indoor sources should also be evaluated as these processes may substantially alter the temporal profiles of airborne concentrations.

Fig. 4 Indoor net emission rates of selected gas-phase PAH in smoking and no-smoking office buildings. See Figure 1 and Table 3 for definitions of abbreviations.

...teps and reduces ...analytes.
...ns discussed above, ...for the analysis of ...H shows consider... ...dy be used for five-... ...PAH. Further develop... ...undertaken as recom... . Recently develope... ...or samples contamin... ...nd wood smoke ha... ...interferences encoun... ...pecificity has also be... ...different programma... ...emission wavelengths ...strated the utility of ... ...model for evaluating ... ...of indoor combustion ...cause ventilation ra... ...door concentrations ... ...ously measured in o... ...e of the sources, it w... ...net emission rates ... ...these sources.
...ns, the gas-phase PAH ...r net emission rates. ...tile gas-phase PAH ha... ...sion rates. In addition ...sion rates for the ga... ...ter for those indoor e...

Acknowledgement

This study was supported by the California Air Resources Board under Contract No. A732-106 and by the Assistant Secretary for Conservation and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under the Contract No. DE-AC03-76SF00098. We especially appreciate the collaboration of the late Joseph Pantalone, the CARB project manager who initiated this project and inspired us all.

References

Arey, J., Atkinson, R., Zielinska, B. and McElroy, P. A. (1989) "Diurnal concentrations of volatile polycyclic aromatic hydrocarbons and nitroarenes during a photochemical air pollution episode in Glendora, California", *Environmental Science and Technology*, **23**, 321-327.

Atkinson, R., Arey, J., Winer, A.M. and Zielinska, B. (1988) *A Survey of Ambient Concentrations of Selected Polycyclic Aromatic Hydrocarbons (PAH) at Various Locations in California*, Final Report, Contract No. A5-185-32, California Air Resources Board, Sacramento, CA.

Cautreels, W. and Van Cauwenberghe, K. (1978) "Experiments on the distribution of organic pollutants between airborne particulate matter and the corresponding gas phase", *Atmospheric Environment*, **12**, 1133-1141.

Daisey, J.M., Spengler, J.D. and Kaarakka, P. (1989) "A comparison of the organic chemical composition of indoor aerosols during woodburing and non-woodburning periods", *Environment International*, **15**, 435-442.

Gundel, L.A., Daisey, J.M. and Offermann, F.J. (1990) "Development of an indoor sampling and analysis method for particulate polycyclic aromatic hydrocarbons". In: Walkinshaw, D.S. (ed.), *Proceedings of Indoor Air '90*, Ottawa, International Conference on Indoor Air Quality and Climate, Vol. 2, 299-305.

Hodgson, A.T., Daisey, J.M. and Offermann, F.J. (1990) "A sampling and analytical method for gas-phase polycyclic aromatic hydrocarbons in indoor air". In: Walkinshaw, D.S. (ed.), *Proceedings of Indoor Air '90*, Ottawa, International Conference on Indoor Air Quality and Climate, Vol. 2, 719-725.

Ju, C. and Spengler, J.D. (1981) "Room-to-room variations in concentrations of respirable particles in residences", *Environmental Science and Technology*, **15**, 592-596.

Ku, H.H. (1969) "Statistical concepts in metrology", In: *Precision Measurement and Calibration, Statistical Concepts and Procedures*, U.S. National Bureau of Standards, NBS Spec. Publ. No. 300, Vol. 1.

Ligocki, M.P. and Pankow, J.F. (1989) "Measurements of the gas/particle distributions of atmospheric organic compounds", *Environmental Science and Technology*, **23**, 75-83.

Loiselle, S.A., Hodgson, A.T. and Offermann, F.J. (1991) "An indoor sampler for polycyclic aromatic compounds", *Indoor Air*, **2**, 191-210.

Miguel, A.H. and Friedlander, S.K. (1978) "Distribution of benzo(a)pyrene and coronene with respect to particle size in Pasadena aerosols in the submicon range", *Atmospheric Environment*, **12**, 2407-2413.

Mumford, J.L., He, X.Z., Chapman, R.S., Cao, S.R., Harris, D.B., Li, X.M., Xian, Y.L., Jiang, W.Z., Xu, C.W., Chuang, J.C., Wilson, W.E. and Cooke, M. (1987) "Lung cancer and indoor air pollution in Xuan Wei, China", *Science*, **235**, 217-220.

Mumford, J.L., Lewtas, J., Burton, R.M., Svendsgaard, D.B., Houk, V.S., Williams, R.W., Walsh, D.B. and Chuang, J.C. (1990) "Unvented kerosene heater emissions in mobile homes: Studies on indoor air particles, semivolatile organics, carbon monoxide, and mutagenicity". In: Walkinshaw, D.S. (ed.), *Proceedings of Indoor Air '90*, Ottawa, International Conference on Indoor Air Quality and Climate, Vol. 2, pp. 257-262.

National Academy of Sciences (1983) *Polycyclic Aromatic Hydrocarbons: Evaluation of Sources and Effects*, Washington, D.C., National Academy Press.

Offermann, F.J. (1988) "Ventilation effectiveness and ADPI measurements of a forced-air heating system", *ASHRAE Transactions*, Vol. 94, Part 1, pp 694-704.

Offermann, F.J., Daisey, J.M., Hodgson, A.T., Gundel, L.A. and Loiselle, S.A. (1990) *Sampling, Analysis, and Data Validation of Indoor Concentrations of Polycyclic Aromatic Hydrocarbons (PAH)*, Final Report, Contract No. A723-106, California Air Resources Board, Sacramento, CA.

Schmeltz, I., Tosk, J. and Hoffman, D. (1976) "Formation and determination of naphthalenes in cigarette smoke", *Analytical Chemistry*, **48**, 645-650.

Tichenor, B.A., Guo, Z., Dunn, J.E., Sparks, L.E. and Mason, M.A. (1991) "The interaction of vapour phase organic compounds with indoor sinks", *Indoor Air*, **1**, 23-35.

Traynor, G.W., Apte, M.G., Carruthers, A.R., Dillworth, J.F., Grimsrud, D.T. and Gundel, L.A. (1987) "Indoor air pollution from wood-burning stoves", *Environmental Science and Technology*, **21**, 691-697.

U.S. Dept. of Health and Human Services (1982) *A Survey of Organic Air Pollutants that have been Tested for Carcinogenicity and Mutagenicity*, U.S. Dept. of Health and Human Services, Public Health Service and National Institutes of Health, NCI Contract No. N01-CP-95607.

Van Vaeck, L. and Van Cauwenberghe, K. (1985) "Characteristic parameters of particle size distributions of primary organic constituents of ambient aerosols", *Environmental Science and Technology*, **19**, 707-716.

Wilson, N.K. and Chuang, J.C. (1991) "Indoor air levels of polynuclear aromatic hydrocarbons and related compounds in an eight-home pilot study". In: Cooke, K., Loening, K. and Merritt, J. (eds), *Polynuclear Aromatic Hydrocarbons: Measurements, Means and Metabolism, Proceedings of the 11th International Symposium on Polynuclear Aromatic Hydrocarbons"*, Columbus, OH, Battelle Press, pp 1053-1064.

Wilson, N.K., Chuang, J.C. and Kuhlman, M.R. (1990) "Sampling semivolatile organic compounds in indoor air". In: Walkinshaw, D.S. (ed.) *Proceedings of Indoor Air '90*, Ottawa, International Conference on Indoor Air Quality and Climate, Vol. 2, 645-650.

Wilson, N.K., Kuhlman, M.R., Chuang, J.C., Mack, G.A. and Howes Jr., J.E. (1989) "A quiet sampler for the collection of semivolatile organic compounds in indoor air", *Environmental Science and Technology*, **23**, 1112-1116.

Zielinska, B., Arey, J., Atkinson, R. and Winer, A.M. (1989) "The nitroarenes of molecular weight in 247 ambient particulate matter samples collected in southern California", *Atmospheric Environment*, **23**, 223-229.