

Characterization of Respirable Suspended Particles and Polycyclic Aromatic Hydrocarbons associated with Environmental Tobacco Smoke

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Abstract

In this study, the concentrations of particulate organic constituents of environmental tobacco smoke (ETS) were determined using an environmental smog chamber, where ETS is the sole source of target compounds. ETS was generated in a 30 m³ environmental chamber by a number of different cigarettes, including the Kentucky 1R4F reference cigarette and eight commercial brands. A total of 12 experimental runs was conducted, and target analytes included a group of ETS markers both in vapor and particulate phase and a class of polycyclic aromatic hydrocarbons (PAHs) associated with ETS particles. The mass concentrations of PAH in ETS particles were also determined. The average contents of benzo (a) pyrene and benzo (a) anthracene in ETS particles for the commercial brands were 12.8 and 21.5 µg/g, respectively. These values are all somewhat higher than those determined previously by other studies. Results from the chamber study are further used to estimate the average and variability of cigarette yields for target compounds associated with ETS. Finally, ratios of RSP to the surrogate standards of UVPM, FPM and solanesol were calculated for each sample. The average conversion factors for the eight commercial brands were 7.3, 38, and 41 for UVPM, FPM, and solanesol, respectively. The UVPM and FPM factors are in good agreement with the recently published values. Whereas there might be a substantial difference in the solanesol content among cigarettes produced in different countries, the variability is somewhat greater than those of UVPM and FPM. Unfortunately, comparison of the PAH yield data from this study with literature values was complicated by a lack of consistency in cigarette smoke generating methodology. Validation of the PAH yields was also difficult due to a lack of information on the ETS related PAH in the literature. From an engineering viewpoint, however, these data on the cigarette yields of ETS components may still provide useful information to studies on the mathematical modeling of indoor air quality management regarding tobacco smoke as a source of interest, or to studies on the assessment of human exposure to ETS.

Key words : Environmental tobacco smoke (ETS), Polycyclic aromatic hydrocarbons (PAH), Nicotine, 3-Ethnlypyridine, Respirable suspended particles (RSP), Benzo (a) pyrene

1. INTRODUCTION

Health significance of human exposure to environ-

mental tobacco smoke (ETS) has been of great concern for several years since ETS is believed to contain many of the same hazardous constituents as mainstream smoke (USEPA, 1992; NRC, 1986). However, the degree to which human exposure to ETS represents an adverse health effect still remains a point of contention

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(Lee and Thornton, 1998; Smith *et al.*, 1992; Lebowitz, 1989; Surgeon General, 1986). This is principally because it is generally known that relative quantities of many individual constituents present in ETS are considerably different from those found in mainstream smoke (Guerin *et al.*, 1987), and also because it is difficult to quantitatively estimate the excess exposure due solely to tobacco smoking in environments most frequently encountered by the general population (Baker and Proctor, 1990; Eatough *et al.*, 1989a).

With the introduction of new and more sensitive analytical methods, an ever-increasing number of smoke constituents is being reported. Until recent years, more than 4,000 individual constituents had been identified in mainstream smoke (Guerin *et al.*, 1992). However, it is difficult to know which of the many components present in ETS are the most hazardous. It is therefore important to analyze ETS for a variety of components comprising both particulate matter and gas-phase constituents.

A class of trace organic constituents of currently greatest concern associated with ETS in the air of indoor environments are volatile organic compounds (VOC) and polycyclic aromatic hydrocarbons (PAH). Some of these constituents are known to be carcinogenic and thus remain of public health concern (Hodgson *et al.*, 1996; Wallace *et al.*, 1987). Results of a chamber study for the characterization of VOC associated with ETS were previously reported in a separate paper (Baek and Jenkins, 1998). PAH are known to be one of the earliest and largest classes of chemical carcinogens. The environmental concern for these compounds is well justified since not only have many of them proven carcinogenic and/or mutagenic properties, but they are also known to be ubiquitous in ambient air, both indoors and outdoors, to which the general public is exposed (Baek *et al.*, 1991a). Excess indoor air concentrations of PAH due to ETS have been determined in a number of studies for real situations defined as smoking and non-smoking environments (Gold *et al.*, 1990; Turk *et al.*, 1987; Elliott and Rowe, 1975). However, despite their importance in estimating the contri-

butions of cigarette smoking to the PAH concentrations in indoor air, very little is known about the amounts of individual PAH compounds included in ETS particles (Vu-Duc and Huynh, 1989).

The purposes of this study are (i) to investigate the occurrence of a wide range of trace organic constituents of ETS, with particular emphasis on PAH associated with ETS particles; and (ii) to characterize the concentrations of selected PAH with respect to appropriate particulate ETS markers such as RSP, UVPM, FPM, and solanesol, respectively. Experimental works were conducted in an environmental chamber where ETS is the sole source of target analytes. ETS was generated by a number of different cigarettes, including the Kentucky reference cigarette and eight different commercial brands. Results from the chamber study were further used to estimate the average and variability of cigarette yields (mass per cigarette) for target compounds associated with ETS.

2. EXPERIMENTAL METHODS

2.1 Environmental chamber

All experiments with cigarette smoke were undertaken in an environmental test chamber at the Oak Ridge National Laboratory (ORNL) in Tennessee. The chamber is a 30 m³ room (3.0 m by 3.7 m, and 2.7 m height), and is consisted of fully automated air processing equipments for temperature, humidity, and sub-ambient pressure control at air circulation flow rates up to 15 m³/hr, which is equivalent to 30 air exchange per hour (ACH). The chamber is constructed with low-emitting materials, and its interior surface is clad with stainless steel. Air supplied to the chamber is dehumidified and then filtered through activated charcoal and high-efficiency particulate air (HEPA) filters to provide low-background concentrations of airborne contaminants. Temperature inside the chamber is controlled by heating and cooling coils located within a re-circulation system, and relative humidity is controlled by addition of steam to recirculated air. The steam is generated through a reverse osmosis water

purification system. The chamber has a wide access door, dual pane windows, and several access ports for instrumental cables, sampling lines, and external power.

2.2 ETS generation

A University of Kentucky reference cigarette (1R4F) and eight commercial cigarette brands were tested for this study. The commercial cigarettes are all filtered brands in regular size (83 mm long), including four 'low-tar', two 'ultra-low-tar', and two 'full-flavor' brands. Two of the 'low-tar' brands were Asian cigarettes; one from Korea and the other from Japan. The other cigarettes were all U.S. brands. Before conducting the experiments, all cigarettes were pre-conditioned for a week at 55~60% RH and room temperature over a solution of saturated sodium bromide in a desiccator (Mahanama and Daisey, 1996).

A total of 12 experimental runs were carried out in this study. In each run, six cigarettes were smoked in the chamber. In order to investigate the proportionality of the amount of ETS generated with the number of cigarettes smoked, two experiments were conducted with three and nine 1R4F reference cigarettes. The results from these runs were compared with those from normal runs with six 1R4F cigarettes smoked. Details of operating conditions for each run are given in Table 1.

Three smoking machines (ADL/II smoking system, Arthur D. Little, Inc., MA, USA) were used simultane-

ously for generating the smoke (i.e., two cigarettes in sequence per machine for six cigarettes smoking). The machine smoking was under a standard condition of 35 cm³ puff, 2 second duration, and one puff per minute (IOS, 1986). Each cigarette was smoked for 8~9 minutes, and approximately 5 cm in length was consumed. The sidestream smoke was emitted into the chamber to simulate ETS, while the mainstream was vented to the outside of the chamber. The smoking machine were placed in the center of the chamber, about 1 m from the floor, surrounded by sampling equipments for ETS constituents. Since the air recirculation system of the chamber was off, it was necessary to use a fan, located in one corner of the chamber, to keep good mixing of the chamber air during the smoke generating period. After finishing the machine smoking, the chamber was left for 5 minutes before sampling started in order to allow the smoke to be completely diluted and mixed in the chamber. ETS sampling then started and continued for nominally 100 minutes for PAH sampling. The fan was switched off during the sampling phase to avoid any substantial deposition of ETS onto the surface of the fan blades.

For the experiments, the chamber was operated in the 'static' mode (i.e., no mechanical ventilation). The only air exchange was due to removal of air for sampling, and the average air exchange rates were estimated to be about 1.45 h⁻¹ for PAH study. Since the chamber is isolated both from the supply air system and the

Table 1. Operating conditions of each individual run for environmental chamber experiments.

Run #	Type of cigarette tested	Number of cigarette smoked	Temperature (°C)	Relative humidity (%)	Air exchange rate (h ⁻¹)	Sampling duration (min)
RUN 1	Reference (1R4F)	6	20~24	48~55	1.42	100
RUN 2	Korean-low tar	6	20~25	46~55	1.43	100
RUN 3	Japanese-low tar	6	20~24	46~55	1.42	100
RUN 4	USA-low tar (I)	6	20~25	47~55	1.92	70
RUN 5	USA-low tar (II)	6	20~25	45~55	1.42	100
RUN 6	USA-ultra low tar (I)	6	20~24	46~55	1.42	100
RUN 7	Reference (1R4F)	6	20~24	46~55	1.13	120
RUN 8	USA-ultra low tar (II)	6	20~24	47~55	1.41	100
RUN 9	Reference (1R4F)	3	20~23	48~55	1.69	80
RUN 10	USA-full flavor (I)	6	20~24	46~55	1.41	100
RUN 11	Reference (1R4F)	9	20~25	45~55	1.41	90
RUN 12	USA-full flavor (II)	6	20~23	46~55	1.41	100

recirculation system, temperature and RH tended to be drift during the chamber experiments depending on the heat load inside the chamber. In order to keep the temperature and RH in the range of 20~25°C and 45~55% during the sampling period, the initial temperature and RH were maintained for each run at 20°C and 55%, respectively. When an experimental run was completed, the chamber was cleaned by supplying air at air exchange rate of 30 ACH for at least 48 hours prior to a subsequent run. Each run was preceded by a background monitoring run for 2 hours to ensure the cleanliness of the chamber. The operating conditions for the background monitoring were same as the main run, except for the smoke generation. The background levels of any target analytes were then subtracted from the measured levels for the main run.

2. 3 Sampling and analytical methods

Target analytes are classified into three major classes: (i) vapor phase ETS markers including 3-EP, nicotine, and myosmine; (ii) particulate phase ETS markers such as respirable suspended particulate matter (RSP), ultraviolet absorbing particulate matter (UV-PM), fluorescing particulate matter (FPM), and solanesol; and (iii) PAH associated with ETS particles.

2. 3. 1 Vapor Phase ETS Markers

For the measurement of vapor phase ETS markers such as 3-EP, nicotine, and myosmine, the chamber air was drawn through glass sorbent tubes containing XAD-4 resin (SKC Inc., PA, USA) using personal pumps at a flow rate of 1 L/min for two hours. After sampling, the flow was rechecked and the average flow before and after sampling was used to calculate the volume of air samples. Two sample tubes were collected for each run, and stored in a freezer at -15°C prior to extraction. The entire content of the XAD-4 sorbent tube was transferred to a 4 ml vial, and then extracted with 2 mL of ethyl acetate containing 0.01% triethylamine and a known amount of quinoline as an internal standard. An aliquot of the extract was injected by an autosampler on a Hewlett-Packard 5890A GC system

equipped with a nitrogen selective detector and a DB-5 capillary column (30 m × 0.32 mm, 1.0 μm). The column oven was initially at 50°C for 1 min, and increased to 215°C at a rate of 10°C/min, and then to 275°C at a rate of 20°C/min. The injector and detector temperatures were set at 220°C and 300°C, respectively. Carrier gas (He) flow was 3.5 mL/min. Peaks for 3-EP, nicotine, and myosmine were determined with one assay and compared to standards of known concentration. 4-EP was used as a surrogate standard for 3-EP since the 3-EP standard material is not commercially available. Details of sampling and analytical performance for the vapor phase ETS markers can be found elsewhere (Baek and Jenkins, 1998).

2. 3. 2 RSP and Particulate Phase ETS Markers

Particle samples were collected simultaneously with other vapor phase samples, and then used for the determination of RSP, UVPM, FPM, and solanesol. RSP sampling was undertaken ducipately inside the chamber by drawing air through a cyclone vortex assembly (Sensidyne Inc., FL, USA) with a cut-off of 3.5 m in diameter and a Fluoropore membrane filter (37 mm, 1.0 μm pore size, Millipore Co., MA, USA) held in a 37 mm plastic filter holder, using a personal pump operating at 2.2 L/min. The mass of RSP in a filter sample was determined gravimetrically, as the difference between the filter mass before and after sample collection. Each filter was conditioned at 20°C and 50% RH for 24 hour before and after sampling in a dark desiccator. Humidity was controlled using a 79.9% (w/w) aqueous solution of glycerol placed in a tray in the bottom of a desiccator cabinet. Prior to weighing, each filter was placed on a dust- and lint-free surface under a static inhibitor (NRD Inc., USA) for about one min. Pre- and post-weighings (5 replicates of each) were carried out on a microbalance (Cahn Instruments, USA) containing another anti-static device attached to the wall inside the weighing chamber.

After the determination of RSP, each particle laden filter was extracted ultrasonically for 30 min in 2 mL of methanol. Replicate analysis of an aliquot of the ex-

tract was performed with a columnless HPLC system, and the UV absorbance was measured at 325 nm. An empty stainless steel tube (1/16" × 50 ft) was used to increase the eluent retention time, with methanol as the mobile phase at 0.8 mL/min. 2, 2', 4, 4'-tetrahydroxybenzophenone (THBP) was used as a surrogate standard for ETS. Determination of FPM was carried out simultaneously with the UVPM determination on the same sample extract. Total sample fluorescence was measured at excitation 300 nm and emission 420 nm using a fluorescence detector connected in a series with the UV detector. Scopoletin was used as a surrogate standard for ETS.

The solanesol content of the methanol extract sample was determined by a reversed phase HPLC system (Hewlett Packard 1,092 II) with a 50 µL sample loop and UV detection at 205 nm, using methanol as the mobile phase at a flow rate of 1.5 mL/min. A spherisorb ODS-2 C18 column (25 cm × 4.6 mm, 5 µm pore size, Sigma-Aldrich Co., USA) was used as an analytical column. The solanesol peak appeared typically at 9.25 min.

Mean duplicate precision for a total of 12 runs was estimated to be 14.1% for RSP, while 14.9%, 11.5%, and 12.5% for UVPM, FPM, and solanesol, respectively. In addition to the gravimetric determination of RSP, real-time measurements of aerosols inside the chamber were carried out throughout all the experimental runs, using a DustTrak (Model 8520, TSI Inc., USA), which is a light scattering aerosol monitor. Aerosol concentration data were logged every two seconds, and then analyzed using the TrakPro Data Analysis Software provided with the instrument. Since the DustTrak readings are not actual gravimetric values, it was used in this study only to provide information on the variation of aerosol levels inside the chamber during the periods of background monitoring, smoke generation and ETS sampling.

2.3.3 PAH associated with ETS Particles

Prior to the determination of PAH in ETS particles, a number of preliminary experiments were undertaken to determine the amount of samples required for the

accurate measurement of PAH by subsequent GC/MS analysis. As a result, it was necessary to use a high volume sampler to collect sufficient amount of ETS particles. In this study, particulate PAH sampling was carried out with a Staplex high volume sampler (Staplex Co., USA), which was mounted on a wall of the chamber through a panel installed for access ports. After generating the cigarette smoke, the ETS particles inside the chamber were collected on 4" diameter fluorocarbon coated glass fiber filters (Pallflex T60A20, Pallflex Products Co., USA) at a flow rate of 700 L/min for nominally 100 mins. Any possible organic contaminants in the filters were removed before use by treating at 400°C for overnight. Prior to and after sampling, each filter was weighed up to 0.01 mg for net particle mass loading after humidity equilibration as described earlier. This allowed the determination of total suspended particulate matter (TSP) associated with ETS. The exposed filters, folded in half with the sample facing inwards, were placed in air sealed plastic envelopes and then stored in the dark refrigerated at -15°C prior to extraction.

The filters containing the ETS particles (typically 45 mg) were extracted with 100 mL of cyclohexane by ultrasonication for 1 hour (Junk and Richard, 1986). Prior to extraction, the particle laden filters were spiked with a known amount of internal standards mixture (1 µg of each). The internal standard mixture (4 mg/mL each) was obtained from Accu Standard Inc. (USA), and then used after dilution to 40 µg/mL. The mixture consisted of 6 deuterated compounds, which are 1, 4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12. In order to ensure sufficient recoveries of organic constituents from the ETS particles, the extraction was repeated with another 100 mL of cyclohexane for 1 hour, and this extract was combined with the first extract. Cyclohexane was preferred as the extraction solvent because it tends to discriminate against many of the interfering extraneous polar substances while retaining efficiency for extracting the neutral PAH fraction, and hence may ease the burden on the subsequent separa-

tion method (Avery *et al.*, 1984; Nielsen, 1979). The extracts, dark yellow solutions, were subsequently concentrated to about 30 mL using a rotary evaporator, and finally evaporated to ca. 5 mL with a stream of oxygen free nitrogen.

The clean-up of extracted samples was performed with Waters Sep-Pak Vac silica cartridges (Millipore Co., USA). Prior to use, each silica cartridge (20 cc, 5 g packed), which was connected onto the Waters Sep-Pak vacuum manifolds, was rinsed with 20 mL of dichloro- methane, and then followed by re-cleaning with 20 mL of pentane at a flow rate of 2 mL/min. The concentrated extract was then loaded onto the cartridge, and the flask containing the residue was rinsed twice with 1 to 2 mL of cyclohexane. These rinsings were also loaded on the the cartridge. After loading the sample, the cartridge was eluted with 10 mL of pentane to remove a non-polar fraction of the extracted organic matter from the cartridge. After discarding the pen-

tane eluent, the cartridge was eluted with 15 mL of 40 % dichloromethane in pentane, which is a more polar solvent, and the eluent containing a semi-polar fraction was collected in a tapered receiving vessel. Subsequently, the cartridge eluent was evaporated slowly to near dryness under a stream of oxygen free nitrogen, and re-dissolved in 0.5 mL of methanol. The sample was then ready for GC analysis. The clean-up method used in this study was in principle based on a method evaluated by Baek *et al.* (1991b).

A total of 16 PAH was identified and quantitated. The PAH standards (a mixture and 16 individual solutions) were obtained from AccuStandard Inc. The GC/MS analysis was performed on a Hewlett-Packard 5970 GC/MS system. A capillary fused silica column (DB-5MS, 0.25 mm × 30 m, 1 µm thickness, J & W Scientific, USA) was used for separation with an oven temperature program as the following: oven was held at the initial temperature (100°C) for 5 min, then in-

Table 2. Selected ion monitoring acquisition parameters for PAH analysis.

Peak No.	Target compound	Abbreviation	Scan start time (min)	Retention time (min)	Selected ion (m/z)	Scan rate (cycle/sec)	Repeat-ability ^{a)} (%)
1	d ₄ -1,4-dichlorobenzene (I.S.)	—	7.00	7.61	150	0.871	—
2	d ₈ -naphthalene (I.S.) ^{b)}	—	10.00	11.28	136	0.418	—
3	Naphthalene	NPTLN	10.50	11.37	128	0.382	24.1%
4	d ₁₀ -acenaphthene	—	14.51	16.09	164	0.352	—
5	Acenaphthalene	ACNPTLN	14.50	15.69	152	0.418	21.5%
6	Acenaphthene	ACNPTN	14.52	16.13	154	0.462	9.3%
7	Fluorene	FLURN	16.50	17.51	166	0.793	14.9%
8	d ₁₀ -phenanthrene (I.S.)	—	19.01	19.94	188	0.293	—
9	Phenanthrene	PHEN	19.02	19.99	178	0.366	20.6%
10	Anthracene	ANTHR	19.03	20.13	178	0.352	13.2%
11	Fluoranthene	FLRTN	22.00	23.07	202	0.793	3.6%
12	Pyrene	PYRN	22.01	23.67	202	0.793	3.7%
13	d ₁₂ -chrysene (I.S.)	—	24.50	26.95	240	0.338	—
14	Benzo (a) anthracene	BaA	24.51	26.89	228	0.326	6.3%
15	Chrysene	CHRY	24.52	27.01	228	0.293	4.4%
16	d ₁₂ -perylene (I.S.)	—	31.02	33.72	264	0.314	—
17	Benzo (b) fluoranthene	BbF	30.00	31.49	252	0.338	4.2%
18	Benzo (k) fluoranthene	BkF	30.01	31.60	252	0.338	5.9%
19	Benzo (e) pyrene ^{c)}	BeP	30.02	32.80	252	0.338	—
20	Benzo (a) pyrene	BaP	31.01	33.34	252	0.326	6.9%
21	Indeno (1, 2, 3-cd) pyrene	I123P	40.00	41.95	276	0.399	5.8%
22	Dibenz (a, h) anthracene	DahA	40.50	42.23	278	0.418	7.9%
23	Benzo (ghi) perylene	BghiP	43.20	44.55	276	0.487	5.5%

^{a)} Repeatability was estimated based on response factors obtained from 4sets of calibration standards.

^{b)} Each internal standard was applied for quantitation of the compounds next to the internal standard.

^{c)} Benzo(e)pyrene was not calibrated since it was not included in the standard mixture.

creased to 300°C at a rate of 10°C/min and held for 25 min at the final temperature. The flow rate of carrier gas (He) was held at 1 mL/min throughout the GC run by an electronic pressure controller with vacuum compensation. The injector temperature was held at 250°C, and the GC/MS transfer line temperature was held at 280°C. In a typical analysis, 2 µl of liquid sample was injected (calibration standards and ETS samples). The injector was set at splitless mode for the initial 2 min, then switched to split mode with vent flow set at 40 mL/min. Electron impact spectra were obtained with an electron energy of 70 eV and an electron multiplier voltage of 2400 V. Mass spectral data were acquired in selected ion monitoring (SIM) mode. Typically, a molecular ion and confirmatory ions were monitored for each compound. In the case where a deuterated internal standard eluted very close to the undeuterated target compounds, molecular ions and confirmatory ions for those compounds were simultaneously monitored in a given group. Detailed SIM acquisition parameters are presented in Table 2. The integrated area of a selected ion was obtained for data manipulation by using the EnviroQuant Software (HP G1032C).

The quantitation of PAH concentrations was conducted by the internal standard method. Four-point calibration curves were constructed for each PAH with concentrations ranging from 1 to 10 µg/mL. The area ratios (target analytes to an associated internal standard) of selected ions were calculated at each concentration level, and then a linear regression curve was fitted to the data to construct calibration curves. Repeatability of the GC/MS analysis was estimated for each PAH using response factor data obtained from the calibration standards, and the results are included in Table 2.

3. RESULTS AND DISCUSSION

3.1 Concentrations of PAH associated with ETS particles

Concentrations of PAH associated with ETS particles are presented in Table 3, together with ETS markers determined simultaneously with PAH. Being sepa-

rated from RSP sampling, the particle samples for PAH analysis were collected by high-volume sampling. As a result, it was not possible to maintain the chamber in static state due to the increased air sampling flow rate. An average air exchange rate of 1.45 h⁻¹ was estimated throughout the PAH study. Therefore, despite the same number of cigarettes smoked for PAH study as the VOC study, the measured levels of ETS markers may not be comparable between the two studies.

The particle samples collected by high-volume sampling was operationally defined in this study as total suspended particulate matter (TSP), being distinguished from RSP by low-volume sampling with a 3.5 µm cut-off cyclone inlet. The average concentrations per cigarette of TSP and RSP determined gravimetrically during the PAH study was 220 µg/m³ and 200 µg/m³, respectively. Despite differences in the sampling flow rate and the location of samplers, concentrations of ETS particles determined by two methods are overall in good agreement (within 10%). However, there was a considerable discrepancy in the measured levels of RSP between the light scattering and gravimetric methods. RSP by the former was about 3.5 times of the latter. Theoretically, TSP concentrations should be greater than those of RSP. In this study, RSP levels appeared to be approximately 90% of TSP concentrations, implying that ETS particles are predominantly associated with fine particles in the respirable range.

The PAH compounds determined in this study, as shown in Table 3, cover a wide range of PAH, from the volatile ones (2 or 3 rings) present mainly in the vapor phase to those (5 rings) found predominantly in the particulate matter in ambient air. These are the most commonly reported PAHs in indoor and ambient air (Guerin *et al.*, 1992; Baek *et al.*, 1991a), although it is not yet clear that such frequent reportings are due to their predominance in the environments or due to the most confident detection by commonly employed analytical methods. A very wide range of concentrations were found for individual PAHs. Among the 16

Table 3. Summary of normalized concentrations of PAH (per cigarette) associated with ETS particles in a 30 m³ environmental chamber.

Analyte	Reference cigarette	Commercial cigarette			
	IR4F (n=4)	Low tar (n=4)	Ultra low tar (n=2)	Full flavor (n=2)	Sub-total (n=8)
	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.
TSP (µg/m ³)	228 ± 12	218 ± 10	212 ± 18	212 ± 6	216 ± 10
PAH (ng/m ³)					
Naphthalene	0.36 ± 0.06	0.31 ± 0.04	0.42 ± 0.14	0.39 ± 0.04	0.36 ± 0.08
Acenaphthalene	0.43 ± 0.10	0.43 ± 0.07	0.33 ± 0.11	0.59 ± 0.01	0.45 ± 0.12
Acenaphthene	0.51 ± 0.06	0.47 ± 0.02	0.44 ± 0.05	0.73 ± 0.05	0.53 ± 0.13
Fluorene	0.52 ± 0.08	0.49 ± 0.07	0.45 ± 0.13	0.61 ± 0.12	0.51 ± 0.10
Phenanthrene	2.34 ± 0.15	1.76 ± 0.46	2.16 ± 0.19	2.35 ± 0.07	2.00 ± 0.41
Anthracene	0.51 ± 0.08	0.40 ± 0.04	0.37 ± 0.10	0.58 ± 0.03	0.44 ± 0.10
Fluoranthene	2.42 ± 0.29	1.95 ± 0.53	1.94 ± 0.46	2.93 ± 0.21	2.19 ± 0.60
Pyrene	2.67 ± 0.34	2.18 ± 0.61	1.92 ± 0.12	2.92 ± 0.06	2.30 ± 0.56
Benzo (a)anthracene	4.56 ± 0.56	4.49 ± 0.47	4.53 ± 0.32	4.99 ± 0.02	4.63 ± 0.40
Chrysene	5.39 ± 0.93	5.87 ± 0.85	5.59 ± 0.52	5.07 ± 0.05	5.60 ± 0.68
Benzo (b)fluoranthene	1.88 ± 0.15	2.10 ± 0.18	2.05 ± 0.08	2.32 ± 0.08	2.14 ± 0.16
Benzo (k)fluoranthene	1.42 ± 0.14	1.23 ± 0.17	1.35 ± 0.13	1.70 ± 0.01	1.38 ± 0.24
Benzo (a)pyrene	2.76 ± 0.29	2.59 ± 0.29	2.70 ± 0.10	3.18 ± 0.03	2.77 ± 0.32
Indeno (1, 2, 3-cd)pyrene	1.36 ± 0.18	1.44 ± 0.17	1.34 ± 0.13	1.54 ± 0.06	1.44 ± 0.15
Dibenz (a, h)anthracene	0.25 ± 0.04	0.28 ± 0.02	0.26 ± 0.05	0.29 ± 0.02	0.28 ± 0.03
Benzo (ghi)perylene	1.61 ± 0.23	1.67 ± 0.26	1.61 ± 0.25	1.80 ± 0.02	1.69 ± 0.21
ETS marker (µg/m ³)					
3-EP	6.9 ± 0.3	5.6 ± 0.4	5.7 ± 0.7	5.7 ± 0.2	5.6 ± 0.4
Nicotine	16.9 ± 2.0	13.8 ± 2.7	11.7 ± 2.9	12.5 ± 4.8	13.0 ± 2.9
Myosmine	1.0 ± 0.3	0.9 ± 0.2	0.9 ± 0.2	0.9 ± 0.3	0.9 ± 0.2
DustTrak-RSP	712 ± 148	702 ± 80	684 ± 58	681 ± 15	692 ± 58
RSP-gravimetric	207 ± 34	202 ± 29	185 ± 20	198 ± 9	197 ± 20
UVP-THBP	29.3 ± 3.9	25.7 ± 4.3	24.4 ± 2.1	25.7 ± 0.9	25.7 ± 3.8
FPM-scopoletine	5.7 ± 0.6	4.6 ± 0.5	5.2 ± 0.3	5.2 ± 0.8	5.2 ± 0.7
Solanesol	4.9 ± 0.8	4.9 ± 0.9	4.8 ± 0.4	4.8 ± 0.2	4.8 ± 0.6

target PAHs, chrysene was the most abundant one, followed by benzo (a) anthracene (BaA) and benzo (a) pyrene (BaP). It is apparent from Table 3 that PAH concentrations for the reference cigarette are in general of the same level as those for the commercial brands. Among commercial brands, full flavors exhibited generally higher concentrations than low-tar and ultra low-tar cigarettes, indicating a possible impact of tar content on PAH emissions. Differently from other runs, three and nine reference cigarettes were tested for the Run #9 and #11, respectively. Results of regression analysis clearly indicated that the measured concentrations of each PAH are proportional to the number of cigarettes smoked in the chamber.

One of the major concerns in studies which address

PAHs in indoor air as a cancer hazard is probably the BaP concentrations. This compound has been known to exhibit a high carcinogenic activity in animal testing and to be at least a suspect human carcinogen (WHO, 1987). In this study, an average concentration of 16.6 ng/m³ of BaP was found in the chamber where six cigarettes were smoked. An early study (Husgafvel-Purssanen *et al.*, 1986) reported 13.3 ng/m³ of BaP concentration in a discotheque-type Finnish restaurant. However, these concentrations are remarkably high levels when compared to a typical range of BaP concentrations found in more commonly encountered environments. A number of studies on indoor PAH samples collected in offices, schools, and residences reported that background levels of BaP typically range from 0.1

to 1 ng/m^3 , while the the similar environments containing ETS range in concentrations from 0.3 to 1.5 ng/m^3 (Gold *et al.*, 1990; Gundel *et al.*, 1990; Turk *et al.*, 1987). Meantime, outdoor air levels of BaP have been most frequently found in the range between $0.05 \sim 0.5 \text{ ng/m}^3$, and occasionally reached $1 \sim 3 \text{ ng/m}^3$ in the United States (Guerin *et al.*, 1992).

3.2 PAH content in ETS particles

A number of studies were conducted to characterize the PAH content in particles associated with tobacco smoking (NRC, 1986; Surgeon General, 1982). However, most of these studies aimed to determine the PAH deliveries from mainstream and sidestream smokes, instead of ETS. In association with ETS chamber study, only a limited number of PAH data is available in the literature for comparison with this study (for example, Vu-Duc and Huynh, 1989). To make matters worse, suitable comparative data are difficult to locate here because of the different cigarettes and smoking regimes employed in the few reported studies. In addition, units for the reported data in the literature were not compatible each other in many cases. For purpose of comparison, it was necessary to convert the PAH concentration data into the amount of PAH in total

particulate matter ($\mu\text{g/g}$) or the amount of PAH emitted per cigarette, as being often reported in the literature. The mass concentrations of PAH associated with ETS particles are summarized in Table 4, while values for the amount of PAH per cigarette are described in a later section of "Estimation of ETS Yields".

From the Table 4, the BaP content in ETS particles appeared to be 12.6 and $12.8 \mu\text{g/g}$ for the reference and commercial cigarettes, respectively. The mass concentration of BaA was found to be $21.6 \mu\text{g/g}$. The BaP and BaA were historically used as indicators for PAH in cigarette smoke condensates in a series of National Cancer Institute studies conducted in 1970's (cited in R.J. Reynolds Tobacco Co., 1988). Reported data in the literature for the mass concentrations of BaP and BaA in particles associated with tobacco smoking are considerably variable. According to a monograph published by R.J. Reynolds Tobacco Co. (1988), the amounts of BaP and BaA in total particulate matter (TPM) associated with sidestream smoke correspond to 8.8 and $11.7 \mu\text{g/g}$, respectively. In another study on the PAH in sidestream smoke (Vu-Duc and Huynh, 1989), the mass concentrations of $4.2 \mu\text{g/g}$ for BaP and $7.3 \mu\text{g/g}$ for BaA can be inferred based on their estimated initial concentrations of TPM, BaP, and BaA in the chamber.

Table 4. A summary of mass concentrations of PAH ($\mu\text{g/g}$) in ETS particles.

Analyte	Reference cigarette	Commercial cigarette			
	1R4F (n=4)	Low tar (n=4)	Ultra low tar (n=2)	Full flavor (n=2)	Sub-total (n=8)
	Mean \pm S.D.	Mean \pm S.D.	Mean \pm S.D.	Mean \pm S.D.	Mean \pm S.D.
Naphthalene	1.5 ± 0.4	1.4 ± 0.2	2.0 ± 0.9	1.9 ± 0.1	1.7 ± 0.5
Acenaphthalene	1.95 ± 0.3	2.0 ± 0.3	1.6 ± 0.4	2.8 ± 0.1	2.1 ± 0.6
Acenaphthene	2.1 ± 0.1	2.2 ± 0.1	2.1 ± 0.4	3.4 ± 0.4	2.5 ± 0.7
Fluorene	2.2 ± 0.2	2.3 ± 0.4	2.1 ± 0.4	2.9 ± 0.5	2.4 ± 0.5
Phenanthrene	10.3 ± 0.1	8.0 ± 1.9	10.2 ± 1.8	11.1 ± 0.0	9.3 ± 2.0
Anthracene	2.1 ± 0.2	1.9 ± 0.2	1.8 ± 0.4	2.7 ± 0.1	2.1 ± 0.5
Fluoranthene	10.1 ± 0.1	8.9 ± 2.2	9.1 ± 1.5	13.8 ± 1.4	10.2 ± 2.8
Pyrene	10.9 ± 0.9	$9.9 \pm .5$	9.0 ± 0.2	13.7 ± 0.2	10.7 ± 2.6
Benzo (a) anthracene	21.6 ± 0.2	20.5 ± 1.7	21.4 ± 3.3	23.5 ± 0.8	21.5 ± 2.2
Chrysene	27.1 ± 0.2	26.8 ± 3.8	26.5 ± 4.6	23.9 ± 1.0	26.0 ± 3.4
Benzo (b) fluoranthene	8.3 ± 0.1	9.6 ± 0.6	9.7 ± 1.2	10.9 ± 0.1	10.0 ± 0.9
Benzo (k) fluoranthene	6.0 ± 0.4	5.6 ± 0.6	6.3 ± 0.1	8.0 ± 0.2	6.4 ± 1.1
Benzo (a) pyrene	12.6 ± 1.1	11.9 ± 1.1	12.8 ± 1.5	15.0 ± 0.3	12.9 ± 1.7
Indeno (1, 2, 3-cd) pyrene	6.3 ± 0.1	6.6 ± 0.7	6.4 ± 1.2	7.3 ± 0.5	6.7 ± 0.8
Dibenz (a, h) anthracene	1.1 ± 1	1.3 ± 0.2	1.2 ± 0.3	1.4 ± 0.1	1.3 ± 0.3
Benzo (ghi) perylene	7.7 ± 0.1	7.7 ± 1.1	7.7 ± 1.8	8.5 ± 0.4	7.9 ± 1.1

These values are all lower than the average contents of BaP and BaA in ETS particles determined from this study. Such significant differences are likely to be associated with several reasons. First of all, there were considerable changes in cigarette manufacturing process during the last decade (Mahanama and Daisey, 1996). For example, raw tobacco tends to be currently treated with more ingredients to reduce the tar levels in mainstream smoke. In addition, smoke generating protocols, degree of air exchange, aging of smoke, and differences in the chamber configuration are all potential factors affecting the measured levels of PAH in different studies. Furthermore a great deal of inconsistency can exist between reported data for PAH emissions from tobacco smoking due to existing differences in selected sampling techniques and/or adopted analytical procedures.

The magnitude of ETS contribution to the concentrations of PAH in indoor air under smoking circumstances has been of great concern for several years. However, quantification of the ETS contribution has not been successfully conducted until recent years largely because these compounds are often difficult to confidently detect in most micro-environments. It is well known that the BaP and other PAH content of indoor air are closely related to the particulate matter content of the air. This is because BaP and other 4~6 ring PAHs are generally found as constituents of airborne particulate matter or as constituents adsorbed on airborne particles.

Several methods have been suggested to identify the anthropogenic sources of PAH and their contributions to atmospheric concentrations of PAH. The classical methods often employed are the PAH profile analysis or characteristic ratios of PAH taken two by two (Daisey *et al.*, 1986; Grimmer *et al.*, 1980; Lee *et al.*, 1976). The term profile represents the relative composition of the mixture of PAH present in a sample. In order to evaluate the compositional differences in PAH profiles, the concentrations of PAH are often standardized into their ratio to a specific PAH. Benzo (e) pyrene (BeP), although it was not determined in this

study, has frequently been selected as a reference PAH because it is not only photochemically stable but also exclusively found in the particulate phase. However, the profile analysis in the literature using characteristic ratios as source identification criteria has revealed apparent discrepancies between those of ambient samples and source emissions (Baek *et al.*, 1991a; Masclat *et al.*, 1986).

The differences may be in general due to interferences from other sources in the ambient samples, or simply due to the differences in sampling and analytical methods in different circumstances. In addition, the discrepancies may also be attributable to the occurrence of physico-chemical modifications of PAH during atmospheric transport or sampling period. A large number of indoor PAH studies (reviewed in Guerin *et al.*, 1992) also reported that concentrations of individual 4~6 ring PAHs present in any given environment at any given time differ from one another by approximately an order of magnitude. All these results imply that there might be no obvious relationship between the relative quantities of individual PAHs present and the environments sampled. It is, therefore, still uncertain whether the relative proportions of some PAH in emissions from a given source type (for example, ETS) may be useful for source discrimination.

Recently, the chemical mass balance (CMB) method has known to be one of dominant approaches to the quantitative apportionment of the sources of particulate matter in ambient air. A key step in the use of CMB method is the determination of the chemical composition of the particulate matter emitted from various sources in a target airshed (Khalili *et al.*, 1995). Such requirements can be a significant drawback in using the CMB model for a particular situation, since the identification of all the sources influencing the concentrations of target compounds and their aerosol characteristics at the receptor site is often difficult to accomplish. An implication of the mass concentration data for a wide range of PAH reported in this study (Table 4) is that these data may be of useful in terms of providing a source fingerprint for ETS particle samples, which is a

crucial requirement of CMB modeling. Not necessarily being related to the CMB method, the information on the amount of PAH in ETS particles themselves can be directly applied to estimating the ETS contribution to the PAH concentrations, once RSP associated with ETS was determined together with PAH from all sources under a given circumstance.

Another alternative method for estimating the fraction of a particulate PAH attributable to ETS is probably using a ratio of a specific ETS marker to each PAH, as being explained in VOC apportionment. In terms of specificity, solanesol has been known to be the best ETS marker present in the particulate phase. A relative contribution of ETS to the concentration of a target PAH can be estimated as following:

$$\% \text{PAH due to ETS} = \frac{F_{\text{solanesol}}/F_{\text{PAH}}}{C_{\text{solanesol}}/C_{\text{PAH}}} \times 100 (\%)$$

where $C_{\text{solanesol}}$ and C_{PAH} indicate the concentrations of solanesol and a target PAH measured in a chamber where ETS is the only source of particulate matter, while $F_{\text{solanesol}}$ and F_{PAH} are the concentrations of those measured in a real environment with a mixture of various sources. According to a large number of literature, solanesol typically makes up 1.6~3.6% of the mass of ETS particles (Nelson *et al.*, 1997, 1998a; Martin *et al.*, 1997; Tang *et al.*, 1990). In this study, the mean contents of solanesol in the ETS particles (based on RSP data) were 2.3% and 2.4% for the reference and commercial cigarettes, respectively, which is also in good agreement with published values.

3.3 Estimation of ETS yields for PAH

Airborne yield of a target compound can be estimated from a direct measurement of the compound present in a particular indoor environment, if physical parameters such as surface characteristics, dimension, and ventilation are known (Lofroth *et al.*, 1989). The yields of ETS components per cigarette are an important factor when evaluating the impact of ETS on indoor air quality since the data can be directly used to estimate the concentrations of ETS components based on the

number of cigarettes smoked and the air exchange rate. During the last two decades, a large number of data have been reported in the literature describing the yields or emission factors of components in tobacco smoke. However, most of them are associated with traditional ETS marker components such as nicotine, particulate matter, carbon monoxide, nitrogen oxides (Nelson *et al.*, 1997, 1998b; Eatough *et al.*, 1989a, b; Lofroth *et al.*, 1989; R.J. Reynolds Tobacco Co., 1988; Guerin *et al.*, 1987), while only a limited number of data are available for trace organic compounds, such as VOCs (Martin *et al.*, 1997) or PAHs (Vu-Duc and Huynh, 1989).

In this study, cigarette yields (in g of target analytes produced per cigarette) were determined for VOCs and PAHs, using an equation derived from a time-dependent mass balance model described by Traynor *et al.* (1985):

$$\text{Yield} = \frac{C_{\text{avg}} V (a+k) t}{N [1 - \text{Exp}\{- (a+k) t\}]}$$

where C_{avg} is the measured average concentration ($\mu\text{g}/\text{m}^3$) in the chamber for the sampling duration, t (h); V is the chamber volume (m^3); N is the number of cigarette smoked in the chamber; a and k are air exchange rate (h^{-1}) and net rate of removal processes other than air exchange (h^{-1}), respectively. The yield estimation using the above equation was based on a number of basic assumptions, as following: (i) cigarette smoking was the only source of the target analytes (i.e., no background contribution); (ii) the concentrations in the chamber followed a first-order exponential decay with time, and the decay was due to the removal of air from the chamber for sampling; (iii) there were no additional losses due to degradation or deposition to the chamber surface, i.e. $k=0$; and finally (iv) the air in the chamber was completely mixed. Although all these assumptions are not possible to be precisely confirmed, they might be roughly ensured by the low background levels and the results of real-time monitoring of RSP in the chamber.

ETS and other air pollutants emitted into an indoor

Table 5. Estimated cigarette yields of PAH (ng per cigarette) associated with ETS particles.

PAH (ng/cigarette)	Reference cigarette	Commercial cigarette			
	1R4F (n=4)	Low tar (n=4)	Ultra low tar (n=2)	Full flavor (n=2)	Sub-total (n=8)
	Mean \pm S.D.	Mean \pm S.D.	Mean \pm S.D.	Mean \pm S.D.	Mean \pm S.D.
Naphthalene	28 \pm 3	24 \pm 3	33 \pm 11	31 \pm 3	28 \pm 6
Acenaphthalene	24 \pm 2	33 \pm 6	26 \pm 9	46 \pm 1	35 \pm 9
Acenaphthene	89 \pm 1	94 \pm 4	91 \pm 10	148 \pm 10	107 \pm 26
Fluorene	33 \pm 3	38 \pm 5	35 \pm 10	48 \pm 9	40 \pm 8
Phenanthrene	143 \pm 42	135 \pm 33	169 \pm 15	184 \pm 5	156 \pm 32
Anthracene	30 \pm 3	31 \pm 3	29 \pm 8	45 \pm 3	34 \pm 8
Fluoranthene	141 \pm 39	150 \pm 39	152 \pm 36	229 \pm 16	170 \pm 47
Pyrene	165 \pm 42	168 \pm 44	150 \pm 9	228 \pm 5	179 \pm 43
Benzo (a) anthracene	366 \pm 15	347 \pm 30	354 \pm 25	391 \pm 1	360 \pm 29
Chrysene	483 \pm 45	453 \pm 61	437 \pm 40	397 \pm 4	435 \pm 50
Benzo (b) fluoranthene	154 \pm 20	163 \pm 11	160 \pm 6	181 \pm 6	167 \pm 12
Benzo (k) fluoranthene	96 \pm 13	95 \pm 11	105 \pm 10	133 \pm 1	107 \pm 19
Benzo (a) pyrene	209 \pm 22	200 \pm 19	211 \pm 7	249 \pm 2	215 \pm 25
Indeno (1,2,3-cd) pyrene	107 \pm 1	111 \pm 12	105 \pm 10	120 \pm 4	112 \pm 11
Dibenz (a, h) anthracene	20 \pm 3	22 \pm 1	20 \pm 4	23 \pm 2	22 \pm 2
Benzo (ghi) perylene	124 \pm 16	129 \pm 18	126 \pm 19	141 \pm 1	131 \pm 15
TSP (mg per cigarette)	16.6 \pm 0.3	16.9 \pm 0.6	16.6 \pm 1.4	16.6 \pm 0.5	16.8 \pm 0.7

environment will be eventually removed from the air by three major routes, i.e. air exchange through ventilation, surface deposition, and chemical transformation. Thus, it can be expected that airborne yields estimated from this study are less than emission factors estimated for sidestream cigarette smoke determined by using a small-volume collecting device surrounding the cigarette tip. The difference will be much greater for components that can easily disappear by processes other than ventilation.

The PAH yields determined for the sidestream ETS particles are presented in Table 5. The average yields of BaP per cigarette were 209 and 215 ng for the reference and commercial cigarettes, respectively. The coefficient of variation for the average yields was about 10%, indicating a good precision for the estimated yield data. The average yield of BaA for the commercial brands appeared to be 360 ng/cigarette, while TSP yield was 16.8 mg/cigarette.

The emission factors reported in the literature for PAH associated with tobaccos smoke are considerably variable. In a Surgeon Generals report (1982), sidestream emission factors for BaP were estimated to be

in the range of 20~140 ng/cigarette, which is significantly lower than the average BaP yield that we determined. However, these values might be highly uncertain since the sidestream emissions were inferred based on published sidestream to mainstream ratios and ranges of mainstream deliveries (Guerin *et al.*, 1986). According to a monograph published by R.J. Reynolds Tobacco Co. (1988), particulate matter associated with sidestream smoke was determined to be 16.9 mg/cigarette, while the amount of BaP and BaA in the sidestream smoke were 147.9 ng and 197.5 ng per cigarette, respectively. The particulate matter yield was nearly equivalent to the TSP yields from this study, but both of BaP and BaA emission factors are only 70% and 55% of those determined in this study, respectively. Validation of the results from this study by comparing them to other literature values is extremely difficult, mainly due to a lack of yield data for PAH in the literature. Thus, further research is required to enlarge the data-base for the validation of PAH yields associated with ETS.

From an engineering viewpoint, nevertheless, these data on the cigarette yields of ETS components may be

useful to studies on the mathematical modeling of indoor air quality management regarding tobacco smoke as a source of interest, or to studies on the assessment of human exposure to ETS in indoor environments. As an example, if the number of smoked cigarettes and the volume of indoor spaces are known, the ventilation rate needed to attain a less toxic level or a comfort level can be approximately calculated.

3.4 ETS–RSP apportionment factors

In this study, UVPM and FPM were determined as the equivalent concentrations of surrogate standards. In order to convert the surrogate concentrations to ETS related RSP equivalent concentrations, conversion factors are necessary, being defined as the ratio of the surrogate standard equivalent concentration to the concentration of ETS related RSP. Likewise, if solanesol

concentrations are to be converted to RSP equivalent concentrations, the ratio of solanesol to ETS–RSP concentrations should be known. By multiplying the corresponding conversion factors to the concentrations of surrogate standards or solanesol, it is possible to apportion the fraction of RSP attributed to ETS (Heavner *et al.*, 1996). Ratios of gravimetric RSP to the surrogate standards and solanesol concentrations were calculated for each sample, and then the results are summarized in Table 6, together with ratios reported in the literature for a wide range of international cigarettes (Nelson *et al.*, 1997, 1998b). In this calculation, concentrations of RSP and particulate ETS markers from both VOC and PAH studies are all utilized because only relative ratios between RSP and other markers are concern.

The average UVPM factors for the reference and commercial cigarettes was 6.8 and 7.3, respectively,

Table 6. Comparison of ratios of RSP to ETS surrogate standards for various type of cigarettes tested from this study and those previously reported in the literature.

Type of cigarette	RSP/UVPM _{THBP}	RSP/FPM _{scopoletin}	RSP/Solanesol	Reference
	Mean ± SD	Mean ± SD	Mean ± SD	
Reference, 1R4F (n = 8)	6.8 ± 0.4	38 ± 3	42 ± 2	This study
Commercial total (n = 16)	7.3 ± 0.5	38 ± 2	41 ± 3	This study
Korean–low tar (n = 2)	7.0 ± 0.4	39 ± 3	41 ± 8	This study
Japanese–low tar (n = 2)	6.9 ± 0.8	36 ± 0	39 ± 5	This study
USA–low tar (n = 4)	7.3 ± 0.6	40 ± 2	41 ± 1	This study
USA–ultra low tar (n = 4)	7.4 ± 0.6	36 ± 1	42 ± 1	This study
USA–full flavor (n = 4)	7.4 ± 0.3	38 ± 3	42 ± 1	This study
USA–total (n = 12)	7.4 ± 0.5	38 ± 3	42 ± 1	This study
Australia	7.3 ± 0.2	43 ± 1	29 ± 1	Nelson <i>et al.</i> (1998)
Brazil	6.8 ± 0.3	40 ± 2	30 ± 1	Nelson <i>et al.</i> (1998)
Canada	7.3 ± 0.3	41 ± 2	68 ± 3	Nelson <i>et al.</i> (1998)
China	7.6 ± 0.3	45 ± 3	53 ± 4	Nelson <i>et al.</i> (1998)
Czech Republic	8.5 ± 0.3	47 ± 2	56 ± 6	Nelson <i>et al.</i> (1997)
England	7.1 ± 0.3	42 ± 2	34 ± 1	Nelson <i>et al.</i> (1998)
France	6.9 ± 0.3	38 ± 2	36 ± 1	Nelson <i>et al.</i> (1997)
Germany	7.8 ± 0.6	43 ± 3	41 ± 2	Nelson <i>et al.</i> (1997)
Hong Kong	8.4 ± 0.8	47 ± 5	38 ± 7	Nelson <i>et al.</i> (1997)
Italy	8.3 ± 0.2	45 ± 2	47 ± 1	Nelson <i>et al.</i> (1997)
Japan	7.1 ± 0.2	42 ± 1	36 ± 3	Nelson <i>et al.</i> (1998)
Korea	7.0 ± 0.4	38 ± 2	35 ± 2	Nelson <i>et al.</i> (1998)
Malaysia	8.1 ± 0.5	44 ± 3	42 ± 3	Nelson <i>et al.</i> (1997)
Portugal	8.9 ± 0.4	47 ± 2	49 ± 2	Nelson <i>et al.</i> (1997)
Spain	8.1 ± 0.7	44 ± 3	44 ± 7	Nelson <i>et al.</i> (1997)
Sweden	8.6 ± 0.6	44 ± 6	41 ± 3	Nelson <i>et al.</i> (1997)
Switzerland	8.2 ± 0.5	43 ± 2	41 ± 3	Nelson <i>et al.</i> (1997)
United States	8.5 ± 0.8	47 ± 4	40 ± 3	Nelson <i>et al.</i> (1997)
United States	7.0 ± 0.2	41 ± 2	30 ± 1	Nelson <i>et al.</i> (1998)

while FPM factors was 38 for both type of cigarettes. The UVPM conversion factor of 7.3 for the commercial brands is in good agreement to recently published values of 7.0 (Nelson *et al.*, 1998) and 7.5 (Heavner *et al.*, 1996). The FPM factor is also close to the previously reported values of 39 (Heavner *et al.*, 1996) and 41 (Nelson *et al.*, 1998a), which were determined for American cigarettes. Thus, despite differences in crop-years and brand styles, there might be a general similarity in the factors for UVPM and FPM among a broad range of cigarettes.

The average ratio of RSP to solanesol for the commercial brands was 41 with a standard deviation of 3. The ratio determined from this study is somewhat higher than has been reported in an international cigarettes study. Recently, Nelson *et al.* (1998a) reported an average value of 30, 35 and 36 for the American, Korean, and Japanese cigarettes, respectively. However, the factor of 40 for the American brands was determined in their previous study (Nelson *et al.*, 1997), which is closer to the ratio determined in this study. The same study also reported an average value of 43 (with a standard deviation of 6) across all the countries investigated. These results imply that there might be substantial differences in the solanesol content among cigarettes produced in different countries, and the variability is somewhat greater than those of UVPM and FPM. In this context, Nelson *et al.* (1998a) suggested that application of country-specific solanesol factors would yield more accurate results rather than using an overall average factor.

Strictly speaking, the cigarette smoke tested in this study can not be regarded as the real ETS since only sidestream smoke was generated and diluted in the environmental chamber. However, it is well known that major part of ETS is contributed by sidestream smoke, and that diluted and aged sidestream smoke generated by cigarette-smoking machines correlates very well to ETS and is widely used as a surrogate for ETS in experimental situations. Thus, results obtained from the chamber experiments carried out in this study may still be useful to provide quantitative information on the

chemical characteristics of ETS, particularly with respect to trace organic constituents including PAHs.

4. SUMMARY AND CONCLUSIONS

In this study, a wide range of PAH associated with ETS particles were determined using an environmental chamber, where ETS is the sole source of target compounds. ETS was generated in a 30 m³ environmental chamber by a number of different cigarettes, including the Kentucky 1R4F reference cigarette and eight commercial brands.

Mass concentrations of PAH in ETS particles were also determined. The average contents of BaP and BaA in ETS particles for the commercial brands were 12.8 and 21.5 µg/g, respectively. These values are all somewhat higher than those determined previously by other studies. An implication of the mass concentration data for a wide range of PAH reported in this study is that these data may be useful in terms of providing a source fingerprint for ETS particles, which is a crucial requirement of chemical mass balance modeling for the apportionment of PAH sources in indoor environments. In addition, the information on the amount of PAH in ETS particles themselves can be directly applied to estimating the ETS contribution to the PAH concentrations, once RSP associated with ETS was determined together with PAH from all sources under a given circumstance.

Results from the chamber study are further used to estimate the average and variability of cigarette yields for target compounds associated with ETS. Unfortunately, comparison of the yield data from this study with other literature values was complicated by a lack of consistency in cigarette smoke generating methodology. Validation of the PAH yields was also difficult due to a lack of information on the ETS related PAH in the literature. From an engineering viewpoint, however, these data on the cigarette yields of ETS components may provide useful information to studies on the mathematical modeling of indoor air quality management regarding tobacco smoke as a source of inter-

est, or to studies on the assessment of human exposure to ETS in indoor environments.

Finally, ratios of RSP to the surrogate standards of UVPM, FPM and solanesol were calculated for each sample. The average conversion factors for the eight commercial brands were 7.3, 38, and 41 for UVPM, FPM, and solanesol, respectively. The UVPM and FPM factors are in good agreement to recently published values, whereas there might be a substantial difference in the solanesol content among cigarettes produced in different countries, and the variability is somewhat greater than those of UVPM and FPM.

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