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Formation of particulate-phase and gas-phase polycyclic aromatic hydrocarbons in cigarette smoke

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Abstract. This study examines the concentrations of particulate-phase polycyclic aromatic hydrocarbons (PAHs) and gas-phase PAHs in sidestream cigarette smoke. Sixteen PAHs were determined for four brands of cigarettes. The volume of the experimental room is approximately 66 m^3. The air samples in the room were collected before and after smoking. The median total of particulate-phase and gas-phase PAH concentrations before smoking 3.13 ng/m^3 and 48.0 ng/m^3, respectively. The median concentrations of them after smoking were 10.0 ng/m^3 and 79.6 ng/m^3. The median increases in the total of 16 PAH concentrations per cigarette during smoking were 271 ng for the particulate-phase PAHs and 1960 ng for the gas-phase PAHs. According to the relationship between particulate-phase and gas-phase PAHs after smoking, the two- to four-ring gas-phase PAHs and the higher molecular weight particulate-phase PAHs were probably formed from similar precursors. The relationship between the total suspended particulate (TSP) concentration and the increase in the total particulate-phase concentration of the 16 PAHs per cigarette during smoking were significantly positive. The increase in the total gas-phase concentration of the 16 PAHs tended to increase as the TSP concentration increased. This may indicates that decreasing the amount of TSP produced inhibit the production of PAHs during smoking.

Keywords: sidestream cigarette smoke; particulate-phase polycyclic aromatic hydrocarbons; gas-phase polycyclic aromatic hydrocarbons; total suspended particulate

1. Introduction

Cigarette smoke is an important source of toxic chemicals to active smokers and those exposed to second-hand smoke. Exposure to cigarette smoke poses risks of developing cancers and various respiratory and cardiovascular diseases (IARC 2004, OEHHA 2005). Evidence that smoking is a major cause of heart disease has been found in many studies (Villablanca *et al.* 2000, Messner and Bernhard 2014). More than 7000 chemicals, including many carcinogens and hazardous chemicals, have been found in cigarette smoke. These constituents of cigarette smoke include polycyclic aromatic hydrocarbons (PAHs) (IARC 2010), which are primarily produced as a result of incomplete combustion of organic material in car engines, incinerators, and factories (Nam *et al.* 2008, Obrist *et al.* 2015, Subramanian *et al.* 2015). Each PAH molecule has two or more fused

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benzenoid rings, and many PAHs have been found to have carcinogenic and mutagenic properties. The International Agency for Research on Cancer has classed benzo[a]pyrene (BaP) as a Group 1 carcinogen (carcinogenic to humans) (IARC 2016). Dibenz[a,h]anthracene (DahA), dibenz[a,j]acridine, and dibenzo[a,l]pyrene are classed as Group 2A carcinogens (probably carcinogenic to humans). Many PAHs, including BaP and benzo[b]fluoranthene (BbF), are also considered to be mutagenic (Luch 2005). Because of their toxicities, PAHs are regulated by governmental bodies in some countries. For example, the US Environmental Protection Agency has included many PAHs in its toxic pollutant and priority pollutant lists, which are applied under the US Clean Water Act (USEPA 2016). Anthracene (Ant) has been included in the European Commission's REACH candidate list (ECHA 2016).

In some experimental studies, PAHs have been found in cigarette smoke (Ding *et al.* 2007, Vu *et al.* 2015). Most of these studies have been focused on PAHs in particulate matter. Little information is available on gaseous PAHs in cigarette smoke. The purpose of the study described here was to investigate both particulate-phase and gas-phase PAHs in sidestream cigarette smoke. In the study, PAH formation processes during smoking and countermeasures to decrease PAH concentrations in cigarette smoke were considered.

2. Materials and methods

2.1 Samples

Four brands of cigarettes were used in this study. The tar and nicotine contents of the cigarettes were 6-19 mg/cigarette and 0.5-1.4 mg/cigarette, respectively. The arithmetic mean filter and leaf weights (n=4) of the cigarettes, before being smoked, were 0.11-0.18 g/cigarette and 0.53-0.59 g/cigarette, respectively. The PAH concentrations in air samples collected before and after cigarettes had been smoked were measured.

Four air samples were collected before and after cigarettes of brands A–D had been smoked. The air sampling room was 2.5 m high, 5.3 m long, and 5.0 m wide, so the volume was approximately 66 m^3. Each air sample collected before cigarettes had been smoked in the sampling room was collected using a high-volume air sampler (HV-500R; Sibata Scientific Technology Ltd., Souka, Japan) over a period of 1.0 h at a flow rate of 400 L/min (giving a sampling volume of 24 m^3). Particulate matter was collected on a quartz fibre filter (QR-100; Advantec, Tokyo, Japan). The filter had a minimum particle collection efficiency of 99.99 % for particles with diameters of 0.3 µm when air was passed through the sampler at a velocity of 5 cm/s. Gas-phase PAHs were collected on two polyurethane foam plugs (080130-0941A; Sibata Scientific Technology Ltd.). After the initial air samples had been collected, the door and windows of the sampling room were left open for about 1 h. The door and windows were then closed, and two cigarettes were smoked in the room. Sidestream smoke samples were collected using the high-volume air sampler over a period of 2.75 h at a flow rate of 400 L/min (giving a sampling volume of 66 m^3). Particulate-phase PAHs were collected on a quartz fibre filter, and gas-phase PAHs were collected on two polyurethane foam plugs. The used filters and polyurethane foam plugs were analysed as described in the analytical methods and instruments section below.

2.2 PAHs

Table 1 Sixteen PAHs measured in this study

PAHs	CAS No.	PAHs	CAS No.
Naphthalene (Nap)	91-20-3	Benzo[*a*]anthracene (BaA)	56-55-3
Acenaphthylene (Acy)	208-96-8	Chrysene (Chr)	218-01-9
Acenaphthene (Ace)	83-32-9	Benzo[*b*]fluoranthene (BbF)	205-99-2
Fluorene (Flu)	86-73-7	Benzo[*k*]fluoranthene (BkF)	207-08-9
Phenanthrene (Phe)	85-01-8	Benzo[*a*]pyrene (BaP)	50-32-8
Anthracene (Ant)	120-12-7	Indeno[1,2,3-cd]pyrene (IP)	193-39-5
Fluoranthene (Flt)	206-44-0	Dibenz[*a,h*]anthracene (DahA)	53-70-3
Pyrene (Pyr)	129-00-0	Benzo[*ghi*]perylene (BP)	191-24-2

The abbreviations in parenthesis are used in this study.

The target compounds were the 16 PAHs shown in Table 1. These PAHs have been detected frequently in various environmental media in many studies (Guo *et al.* 2007, Li *et al.* 2017, Menichini *et al.* 2007, Nam *et al.* 2008, Romagnoli *et al.* 2016). The US Environmental Protection Agency regulates the concentrations of these 16 PAHs in air, water, and soil. Naphthalene (Nap) is a two-ring PAH. Acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), and Ant are three-ring PAHs. Fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), and chrysene (Chr) are four-ring PAHs. BbF, benzo[k]fluoranthene (BkF), BaP, and DahA are five-ring PAHs. Indeno[1,2,3-cd]pyrene (IP) and benzo[ghi]perylene (BP) are six-ring PAHs.

2.3 Analytical methods and instruments

Each quartz fibre filter was weighed using an electronic balance before and after use. Each filter that had been used to sample air after cigarettes had been smoked was cut into 16 portions, which were placed in a 260 mL bottle and extracted with 100 mL of a mixture of hexane and dichloromethane for 15 min in an ultrasonic bath. The extract was concentrated to 3 mL using a rotary evaporator, then passed through a disposable filter (Whatman PURADISCTM 25TF; GE Healthcare Bio-Sciences, Pittsburgh, PA, USA). The extract was then concentrated to 1.5 mL under flowing N_2, then 200 μL of an internal standard mixture were added, and hexane was added to bring the final volume to 2 mL.

Two polyurethane foam plugs were used in each experiment. Each polyurethane foam plug that had been used to sample air after cigarettes had been smoked was cut into 16 portions, which were placed in a 260 mL bottle and extracted with 220 mL of hexane for 15 min in an ultrasonic bath. The separate extracts of the two foam plugs were each concentrated to 3 mL using a rotary evaporator and then mixed together. The extract was then passed through a disposable filter and concentrated to 1.5 mL under flowing N_2, then 200 μL of an internal standard mixture were added, and hexane was added to bring the final volume to 2 mL.

The PAH concentrations in the extracts were determined by gas chromatography-mass spectrometry (using a 5975B inert XL E/CI MSD instrument; Agilent Technologies, Santa Clara, CA, USA). The instrument was equipped with a HP-5MS capillary column (30 m long, 0.25 mm i.e., 0.25 μm film thickness; Agilent Technologies). The gas chromatograph was using in splitless injection mode, with a sample volume of 2 μL and an injection port temperature of 250℃. The

oven temperature programme started at 70℃ (held for 1.5 min), then increased at 20℃/min to 180℃, then increased at 5 ℃/min to 280℃ (held for 1 min). The carrier gas was helium. The mass spectrometer was operated in electron impact ionization mode, and the electron energy was 70 eV. Each analyte was identified using two representative fragment ions then quantified using the most abundant fragment ion. Quantification was performed using an internal standard calibration method using standards containing the 16 PAHs shown in Table 1 (TCL PAH Mix, CRM48905; Supelco, Bellefonte, PA, USA) and three deuterated PAHs (525 Fortification Solution, 48230-U; Supelco).

The total suspended particulate (TSP) concentration was defined as the difference between the weight of a quartz fibre filter before and after being used to sample air divided by 24 m^3 for a sample collected before cigarettes had been smoked or 66 m^3 for a sample collected after cigarettes had been smoked.

Table 2 Particulate-phase PAHs in air samples before smoking

	Brand A	Brand B	Brand C	Brand D	All brands
Nap	1.05 (3/4) [N.D. – 1.90]	0.97 (4/4) [0.78 – 1.16]	0.92 (4/4) [0.63 – 1.78]	2.40 (4/4) [1.72 – 3.38]	1.09 (15/16) [N.D. – 3.38]
Acy	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/16) [N.D.]
Ace	N.D. (1/4) [N.D. – 0.38]	N.D. (1/4) [N.D. – 0.15]	N.D. (1/4) [N.D. – 0.31]	0.70 (4/4) [0.15 – 0.75]	N.D. (7/16) [N.D. – 0.75]
Flu	0.037 (2/4) [N.D. – 0.17]	N.D. (1/4) [N.D. – 0.11]	0.071 (3/4) [N.D. – 0.14]	0.11 (3/4) [N.D. – 0.12]	0.058 (9/16) [N.D. – 0.17]
Phe	0.078 (3/4) [N.D. – 0.19]	0.16 (4/4) [0.062 – 0.25]	0.18 (4/4) [0.026 – 0.28]	0.13 (3/4) [N.D. – 0.33]	0.12 (14/16) [N.D. – 0.33]
Ant	0.12 (3/4) [N.D. – 0.19]	0.070 (3/4) [N.D. – 0.22]	0.038 (2/4) [N.D. – 0.19]	0.023 (2/4) [N.D. – 0.19]	0.051 (10/16) [N.D. – 0.22]
Flt	0.090 (4/4) [0.020 – 0.17]	0.11 (4/4) [0.016 – 0.34]	0.068 (3/4) [N.D. – 0.085]	0.082 (4/4) [0.019 – 0.28]	0.078 (15/16) [N.D. – 0.34]
Pyr	0.14 (3/4) [N.D. – 0.62]	0.13 (4/4) [0.058 – 0.18]	0.050 (3/4) [N.D. – 0.13]	0.13 (4/4) [0.036 – 0.45]	0.094 (14/16) [N.D. – 0.62]
BaA	0.095 (4/4) [0.070 – 0.12]	0.11 (3/4) [N.D. – 0.19]	0.075 (4/4) [0.038 – 0.12]	0.12 (3/4) [N.D. – 0.56]	0.089 (14/16) [N.D. – 0.56]
Chr	0.087 (4/4) [0.064 – 0.20]	0.13 (4/4) [0.078 – 0.53]	0.054 (4/4) [0.038 – 0.14]	0.087 (3/4) [N.D. – 0.63]	0.091 (15/16) [N.D. – 0.63]
BbF	0.27 (4/4) [0.20 – 0.37]	0.30 (3/4) [N.D. – 0.52]	0.20 (3/4) [N.D. – 0.25]	0.43 (4/4) [0.28 – 0.86]	0.28 (14/16) [N.D. – 0.86]
BkF	0.37 (4/4) [0.14 – 0.77]	0.51 (4/4) [0.18 – 0.81]	0.46 (4/4) [0.23 – 1.16]	2.00 (4/4) [1.49 – 2.63]	0.57 (16/16) [0.14 – 2.63]
BaP	N.D. (1/4) [N.D. – 0.50]	0.30 (3/4) [N.D. – 0.68]	0.14 (2/4) [N.D. – 0.35]	0.45 (3/4) [N.D. – 1.00]	0.26 (9/16) [N.D. – 1.00]
IP	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D. – 0.75]	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D. – 1.81]	N.D. (2/16) [N.D. – 1.81]
DahA	N.D. (1/4) [N.D. – 0.32]	N.D. (1/4) [N.D. – 0.57]	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D. – 1.70]	N.D. (3/16) [N.D. – 1.70]
BP	0.095 (2/4) [N.D. – 1.70]	N.D. (1/4) [N.D. – 0.68]	N.D. (1/4) [N.D. – 0.73]	N.D. (1/4) [N.D. – 2.20]	N.D. (5/16) [N.D. – 2.20]

Table 2 Continued

	Brand A	Brand B	Brand C	Brand D	All brands
Σ16 PAHs	2.15 (4/4) [1.71 – 6.91]	3.00 (4/4) [1.46 – 6.43]	2.74 (4/4) [1.35 – 4.26]	7.17 (4/4) [6.28 – 13.2]	3.13 (16/16) [1.35 – 13.2]

The upper values show median concentration (detection rate: the number of detected samples / the number of all measured samples) and the lower values show [concentration range]. All units are ng/m^3. N.D. means Not detected. Σ16 PAHs means total PAH concentrations.

Table 3 Gas-phase PAHs in air samples before smoking

	Brand A	Brand B	Brand C	Brand D	All brands
Nap	35.6 (4/4) [12.5 – 58.8]	16.3 (4/4) [0.76 – 32.3]	15.9 (4/4) [14.1 – 21.3]	14.6 (4/4) [9.24 – 24.3]	14.9 (16/16) [0.76 – 58.8]
Acy	8.00 (4/4) [1.63 – 18.1]	3.72 (4/4) [0.19 – 9.24]	1.58 (4/4) [1.45 – 2.32]	1.32 (4/4) [1.00 – 1.57]	1.60 (16/16) [0.19 – 18.1]
Ace	4.78 (4/4) [2.19 – 8.15]	0.11 (3/4) [N.D. – 5.15]	2.32 (4/4) [1.34 – 3.26]	2.58 (4/4) [1.54 – 3.19]	2.58 (15/16) [N.D. – 8.15]
Flu	20.2 (4/4) [4.48 – 48.2]	14.4 (4/4) [0.62 – 34.9]	5.15 (4/4) [3.11 – 5.40]	4.85 (4/4) [3.30 – 6.74]	5.21 (16/16) [0.62 – 48.2]
Phe	17.5 (4/4) [10.7 – 29.9]	26.2 (4/4) [23.5 – 32.4]	13.7 (4/4) [7.39 – 16.5]	12.0 (4/4) [8.25 – 19.0]	16.6 (16/16) [7.39 – 32.4]
Ant	0.26 (3/4) [N.D. – 0.56]	0.65 (2/4) [N.D. – 1.46]	0.38 (3/4) [N.D. – 0.59]	0.066 (2/4) [N.D. – 0.30]	0.19 (10/16) [N.D. – 1.46]
Flt	2.03 (4/4) [1.38 – 2.92]	3.13 (4/4) [2.87 – 3.42]	1.60 (4/4) [0.90 – 1.72]	1.27 (4/4) [0.88 – 1.89]	1.76 (16/16) [0.88 – 3.42]
Pyr	0.70 (3/4) [N.D. – 3.36]	3.59 (4/4) [3.44 – 3.98]	1.86 (4/4) [1.21 – 2.28]	1.15 (4/4) [0.029 – 1.80]	1.74 (15/16) [N.D. – 3.98]
BaA	N.D. (1/4) [N.D. – 0.066]	0.093 (4/4) [0.085 – 0.15]	4.47 (4/4) [3.72 – 5.26]	7.47 (4/4) [2.84 – 9.51]	1.49 (13/16) [N.D. – 9.51]
Chr	N.D. (1/4) [N.D. – 0.090]	0.080 (3/4) [N.D. – 0.50]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (4/16) [N.D. – 0.50]
BbF	N.D. (1/4) [N.D. – 0.28]	0.27 (3/4) [N.D. – 0.63]	0.020 (2/4) [N.D. – 0.29]	N.D. (1/4) [N.D. – 0.17]	N.D. (7/16) [N.D. – 0.63]
BkF	N.D. (1/4) [N.D. – 0.58]	0.83 (3/4) [N.D. – 1.30]	0.63 (4/4) [0.036 – 2.97]	1.44 (4/4) [0.98 – 2.13]	0.68 (12/16) [N.D. – 2.97]
BaP	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D. – 1.13]	0.085 (2/4) [N.D. – 0.49]	N.D. (0/4) [N.D.]	N.D. 3(/16) [N.D. – 1.13]
IP	N.D. (0/4) [N.D.]	0.33 (3/4) [N.D. – 0.40]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (3/16) [N.D. – 0.40]
DahA	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/16) [N.D.]
BP	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D. – 0.70]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (1/16) [N.D. – 0.70]
Σ16 PAHs	90.9 (4/4) [34.8 – 166]	74.8 (4/4) [39.4 – 109]	45.9 (4/4) [44.6 – 54.6]	52.3 (4/4) [29.4 – 57.9]	48.0 (16/16) [29.4 – 166]

The upper values show median concentration (detection rate: the number of detected samples / the number of all measured samples) and the lower values show [concentration range]. All units are ng/m^3. N.D. means Not detected. Σ16 PAHs means total PAH concentrations.

3. Results and discussion

3.1 PAHs in air samples before smoking

As can be seen from Table 2, 15 PAHs were detected in the particulate-phase air samples collected before cigarettes had been smoked. BkF was detected in all 16 samples, and Nap, Phe, Flt, Pyr, BaA, Chr, and BbF were detected in almost all of the samples. Nap was the most abundant PAH, and its median and maximum concentrations were 1.09 and 3.38 ng/m^3, respectively. The total PAH concentrations ranged from 1.35 to 13.2 ng/m^3, and the median was 3.13 ng/m^3. The mean mole ratios for the individual PAHs in the particulate samples were 53.5 % for Nap, 14.2 % for BkF, 7.1 % for BbF, 6.6 % for BaP, 4.3 % for Phe, 2.9 % for Pyr, 2.5 % for BaA and Chr, 2.4 % for Flt, 2.2 % for Flu, and 1.8 % for Ant.

As can be seen from Table 3, 15 PAHs were detected in the gas-phase air samples collected before cigarettes had been smoked. Nap, Acy, Flu, Phe, and Flt were detected in all 16 samples. Ace, Pyr, and BaA were detected in almost all of the samples. Phe was the most abundant PAH. The Phe concentrations ranged from 7.39 to 32.4 ng/m^3, and the median was 16.6 ng/m^3. The total PAH concentrations ranged from 29.4 to 166 ng/m^3, and the median was 48.0 ng/m^3. The gas-phase PAH concentrations were much higher than the particulate-phase PAH concentrations. The mean mole ratios for the individual PAHs were 35.2% for Phe, 32.6% for Nap, 11.1% for Flu, 5.5% for Ace, 3.7% for Flt, 3.6% for Pyr, 3.5% for Acy, 3.1% for BaA, 1.4% for BkF, and 0.4% for Ant.

Table 4 Particulate-phase PAHs in air samples after smoking

	Brand A	Brand B	Brand C	Brand D	All brands
Nap	0.38 (4/4) [0.16 – 0.55]	0.44 (4/4) [0.33 – 0.55]	0.49 (4/4) [0.40 – 0.75]	0.81 (4/4) [0.36 – 1.35]	0.49 (16/16) [0.16 – 1.35]
Acy	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/16) [N.D.]
Ace	0.046 (2/4) [N.D. – 0.095]	0.008 (2/4) [N.D. – 0.063]	0.065 (4/4) [0.048 – 0.15]	0.18 (4/4) [0.077 – 0.35]	0.070 (12/16) [N.D. – 0.35]
Flu	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/16) [N.D.]
Phe	N.D. (0/4) [N.D.]	0.041 (2/4) [N.D. – 0.093]	0.027 (3/4) [N.D. – 0.13]	0.040 (2/4) [N.D. – 0.096]	N.D. (7/16) [N.D. – 0.13]
Ant	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D. – 0.18]	N.D. (0/4) [N.D.]	0.035 (2/4) [N.D. – 0.20]	N.D. (3/16) [N.D. – 0.20]
Flt	0.034 (3/4) [N.D. – 0.048]	0.072 (3/4) [N.D. – 0.084]	0.086 (4/4) [0.049 – 0.14]	0.11 (4/4) [0.049 – 0.13]	0.066 (14/16) [N.D. – 0.14]
Pyr	0.11 (3/4) [N.D. – 0.17]	0.044 (3/4) [N.D. – 0.076]	0.045 (4/4) [0.038 – 0.055]	0.065 (4/4) [0.043 – 0.13]	0.050 (14/16) [N.D. – 0.17]
BaA	0.048 (2/4) [N.D. – 0.20]	0.84 (4/4) [0.63 – 1.47]	1.21 (4/4) [0.68 – 1.77]	1.93 (4/4) [0.65 – 5.97]	0.84 (14/16) [N.D. – 5.97]
Chr	0.36 (4/4) [0.18 – 0.49]	1.56 (4/4) [1.47 – 2.51]	2.36 (4/4) [1.56 – 3.30]	2.50 (4/4) [1.43 – 5.41]	1.58 (16/16) [0.18 – 5.41]
BbF	1.10 (4/4) [0.97 – 1.33]	1.75 (4/4) [1.48 – 1.97]	1.69 (4/4) [1.52 – 1.87]	1.93 (4/4) [1.57 – 2.86]	1.63 (16/16) [0.97 – 2.86]

Table 4 Continued

	Brand A	Brand B	Brand C	Brand D	All brands
BkF	0.28 (4/4) [0.21 – 0.44]	0.39 (4/4) [0.35 – 0.46]	0.45 (4/4) [0.35 – 0.57]	0.62 (4/4) [0.46 – 1.30]	0.44 (16/16) [0.21 – 1.30]
BaP	1.71 (4/4) [1.56 – 2.04]	1.99 (4/4) [1.75 – 2.26]	2.18 (4/4) [1.71 – 2.43]	2.14 (4/4) [1.85 – 2.90]	2.00 (16/16) [1.56 – 2.90]
IP	1.14 (4/4) [0.96 – 1.37]	1.17 (4/4) [1.04 – 1.49]	1.26 (4/4) [0.93 – 1.53]	1.34 (4/4) [1.12 – 1.56]	1.17 (16/16) [0.93 – 1.56]
DahA	0.092 (2/4) [N.D. – 0.24]	0.24 (4/4) [0.19 – 0.37]	0.22 (3/4) [N.D. – 0.30]	N.D. (0/4) [N.D.]	0.18 (9/16) [N.D. –0.37]
BP	1.18 (4/4) [0.86 – 1.96]	1.22 (4/4) [0.93 – 1.47]	1.12 (4/4) [0.77 – 1.45]	1.31 (4/4) [0.99 – 1.50]	1.31 (16/16) [0.77 – 1.96]
Σ 16 PAHs	6.58 (4/4) [5.71 – 7.89]	9.70 (4/4) [8.79 – 12.5]	11.6 (4/4) [8.65 – 13.0]	12.6 (4/4) [9.74 – 23.4]	10.0 (16/16) [5.71 – 23.4]

The upper values show median concentration (detection rate: the number of detected samples / the number of all measured samples) and the lower values show [concentration range]. All units are ng/m^3. N.D. means Not detected. Σ16 PAHs means total PAH concentrations.

Table 5 Gas-phase PAHs in air samples after smoking

	Brand A	Brand B	Brand C	Brand D	All brands
Nap	7.92 (4/4) [5.80 – 9.55]	14.8 (4/4) [11.6 – 24.2]	11.3 (4/4) [9.92 – 15.2]	12.1 (4/4) [9.70 – 15.1]	11.2 (16/16) [5.80 – 24.2]
Acy	3.83 (4/4) [3.65 – 5.63]	12.2 (4/4) [8.40 – 22.1]	7.41 (4/4) [5.39 – 10.1]	7.42 (4/4) [5.80 – 14.5]	7.42 (16/16) [3.65 – 22.1]
Ace	1.72 (3/4) [N.D. – 2.01]	4.42 (4/4) [3.34 – 6.11]	3.46 (4/4) [3.08 – 4.49]	4.13 (4/4) [4.08 – 5.05]	3.81 (15/16) [N.D. – 6.11]
Flu	7.89 (4/4) [6.46 – 13.7]	19.7 (4/4) [15.9 – 27.6]	9.37 (4/4) [8.83 – 11.3]	13.1 (4/4) [9.19 – 17.5]	11.9 (16/16) [6.46 – 27.6]
Phe	24.0 (4/4) [12.1 – 32.9]	31.3 (4/4) [24.6 – 33.3]	25.1 (4/4) [20.6 – 30.2]	32.0 (4/4) [25.0 – 42.5]	28.7 (16/16) [12.1 – 42.5]
Ant	3.07 (4/4) [1.47 – 4.18]	5.03 (4/4) [3.93 – 5.76]	4.93 (4/4) [3.26 – 5.59]	5.37 (4/4) [4.58 – 8.42]	4.75 (16/16) [1.47 – 8.42]
Flt	4.25 (4/4) [1.99 – 5.86]	6.50 (4/4) [4.88 – 6.72]	5.30 (4/4) [4.07 – 6.37]	6.39 (4/4) [5.26 – 9.26]	5.74 (16/16) [1.99 – 9.26]
Pyr	3.92 (4/4) [1.72 – 5.02]	4.91 (4/4) [3.66 – 5.05]	3.89 (4/4) [2.81 – 4.67]	4.78 (4/4) [3.58 – 7.35]	4.38 (16/16) [1.72 – 7.35]
BaA	0.41 (3/4) [N.D. – 0.80]	0.95 (4/4) [0.68 – 1.07]	0.90 (3/4) [N.D. – 2.20]	1.35 (3/4) [N.D. – 4.24]	0.82 (13/16) [N.D. – 4.24]
Chr	0.70 (3/4) [N.D. – 1.37]	1.14 (3/4) [N.D. – 1.62]	0.66 (3/4) [N.D. – 1.52]	1.07 (4/4) [0.15 – 1.49]	0.93 (13/16) [N.D. – 1.62]
BbF	N.D. (0/4) [N.D.]	0.10 (4/4) [0.068 – 0.16]	0.038 (2/4) [N.D. – 0.13]	N.D. (1/4) [N.D. – 0.085]	N.D. (7/16) [N.D. – 0.16]
BkF	N.D. (0/4) [N.D.]	0.28 (4/4) [0.12 – 0.31]	0.31 (3/4) [N.D. – 1.20]	0.78 (4/4) [0.58 – 1.20]	0.28 (11/16) [N.D. – 1.20]
BaP	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D. – 0.071]	0.042 (2/4) [N.D. – 0.090]	N.D. (0/4) [N.D.]	N.D. (3/16) [N.D. – 0.090]
IP	N.D. (1/4) [N.D. – 0.088]	0.065 (3/4) [N.D. – 0.12]	N.D. (1/4) [N.D. – 0.44]	N.D. (0/4) [N.D.]	N.D. (5/16) [N.D. – 0.44]

Table 5 Continued

	Brand A	Brand B	Brand C	Brand D	All brands
DahA	N.D. (1/4) [N.D. – 0.040]	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D. – 0.39]	N.D. (0/4) [N.D.]	N.D. (2/16) [N.D. – 0.39]
BP	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D. – 0.53]	N.D. (0/4) [N.D.]	N.D. (1/16) [N.D. – 0.53]
Σ 16 PAHs	58.0 (4/4) [35.5 – 78.3]	102 (4/4) [80.9 – 128]	74.0 (4/4) [58.6 – 91.0]	87.9 (4/4) [70.9 – 125]	79.6 (16/16) [35.5 – 128]

The upper values show median concentration (detection rate: the number of detected samples / the number of all measured samples) and the lower values show [concentration range]. All units are ng/m^3. N.D. means Not detected. Σ16 PAHs means total PAH concentrations.

3.2 PAHs in air samples after smoking

As can be seen from Table 4, 14 PAHs were detected in the particulate-phase air samples collected after cigarettes had been smoked. Nap, Chr, BbF, BkF, Bap, IP, and BP were detected in all 16 samples. Flt, Pyr, and BaA were detected in almost all of the samples. BaP was the most abundant PAH. The BaP concentrations ranged from 1.56 to 2.90 ng/m^3, and the median was 2.00 ng/m^3. BaP has been used as an indicator of general PAH mixtures emitted from coking ovens and from similar combustion processes in urban air. It has been found that the benzene-soluble fraction of emissions from coking ovens have contained 0.71 % BaP, and this was used to estimate that the unit risk for BaP as an indicator PAHs in air was 8.7×10^{-5} ng/m^3 (WHO 1987). The lifetime respiratory cancer risk for the median BaP concentration was approximately 1.7×10^{-4}. The total PAH concentrations ranged from 5.71 to 23.4 ng/m^3, and the median was 10.0 ng/m^3. The mean mole ratios for the individual PAHs were 20.1% for BaP, 16.7 % for BbF, 16.2% for Chr, 12.9% for BP, 11.7% for IP, 8.7% for BaA, 5.4% for Nap, 4.5% for BkF, 1.% for DahA, 0.8% for Ace, 0.7% for Flt, and 0.5% for Pyr.

As can be seen from Table 5, all 16 PAHs were detected in the gas-phase air samples collected after cigarettes had been smoked. Nap, Acy, Flu, Phe, Ant, Flt, and Pyr were detected in all 16 samples. Ace, BaA, and Chr were detected in almost all of the samples. Phe was the most abundant PAH. The Phe concentrations ranged from 12.1 to 42.5 ng/m^3, and the median was 28.7 ng/m^3. The total PAH concentrations ranged from 35.5 to 128 ng/m^3, and the median was 79.6 ng/m^3. The mean mole ratios for the individual PAHs were 35.7% for Phe, 15.0% for Flu, 14.4% for Nap, 9.4% for Acy, 7.0% for Flt, 5.9% for Ant, 5.3% for Pyr, 4.8% for Ace, 1.1% for Chr, 1.0% for BaA, and 0.3% for BkF.

3.3 PAH formation while smoking

The correlation coefficients for the relationships between the concentrations of the different PAHs in the particulate-phase and gas-phase air samples collected before cigarettes had been smoked were determined. Some of the correlation coefficients were significant. Correlation coefficients mean pearson coefficients for correlations.

For the particulate-phase samples collected before cigarettes had been smoked, the correlation coefficients for the relationships between the BaA, Chr, and BbF concentrations were > 0.89 ($p < 0.001$: significance level of 1%), and the correlation coefficients for the relationships between the

Table 6 Pearson coefficients for correlations between the particulate-phase PAHs in air samples after smoking

	Nap	Ace	Flt	Pyr	BaA	Chr	BbF	BkF	BaP	IP	DahA
Ace	0.95										
Flt	0.00	-0.11									
Pyr	-0.45	-0.18	-0.29								
BaA	0.79	0.70	-0.01	-0.38							
Chr	0.71	0.56	0.17	-0.51	0.92						
BbF	0.70	0.61	0.27	-0.43	0.88	0.93					
BkF	0.94	0.92	0.01	-0.46	0.88	0.81	0.81				
BaP	0.54	0.43	0.10	-0.51	0.76	0.81	0.80	0.74			
IP	0.19	0.06	0.19	-0.32	0.48	0.46	0.48	0.42	0.82		
DahA	-0.28	-0.19	0.51	-0.15	-0.12	-0.04	0.48	0.13	0.41	0.31	
BP	0.04	0.03	0.07	-0.31	0.50	0.07	0.17	0.22	0.56	0.72	0.69

2-ring PAHs; Nap, 3-ring PAHs; Ace, 4-ring PAHs; Flt, Pyr, BaA, and Chr, 5-ring PAHs; BbF, BkF, BaP, and DahA, 6-ring PAHs; IP and BP. Double line and wavy line represent $p < 0.001$ (significance level of 1%) and $p<0.005$ (significance level of 5%). The PAH abbreviations are shown in the introduction and section 2.2.

Table 7 Pearson Coefficients for Correlations between the gas-phase PAHs in air samples after smoking

	Nap	Acy	Ace	Flu	Phe	Ant	Flt	Pyr	BaA	Chr
Acy	0.92									
Ace	0.90	0.87								
Flu	0.88	0.90	0.82							
Phe	0.52	0.46	0.67	0.58						
Ant	0.62	0.61	0.77	0.54	0.86					
Flt	0.62	0.59	0.77	0.62	0.97	0.95				
Pyr	0.50	0.52	0.58	0.54	0.92	0.86	0.93			
BaA	0.27	0.35	0.49	0.19	0.68	0.81	0.75	0.83		
Chr	0.01	-0.25	0.01	0.12	0.27	-0.12	0.12	-0.01	-0.42	
BkF	-0.11	-0.15	0.04	-0.34	0.10	0.49	0.18	0.18	0.37	-0.54

2-ring PAHs; Nap, 3-ring PAHs; Ace Acy, Flu, Phe, and Ant, 4-ring PAHs; Flt, Pyr, BaA, and Chr, 5-ring PAHs; BkF. Double line and wavy line represent $p<0.001$ (significance level of 1%) and $p<0.005$ (significance level of 5%). The PAH abbreviations are shown in the introduction and section 2.2.

BaP and Pyr concentrations and the BaA, Chr, and BbF concentrations were>0.84 ($p<0.001$). The correlation coefficients for the relationships between the Nap and Ace concentrations and between the Nap and BbF concentrations were 0.81 and 0.78, respectively. For the gas-phase samples collected before cigarettes had been smoked, the correlation coefficients for the relationships between the Nap, Acy, Ace, and Flu concentrations were>0.90 ($p<0.001$) and the correlation coefficients for the relationships between the Phe and Ant concentrations and the Flt and Pyr concentrations were>0.59. The correlations between the BaA concentration and the Phe, Ant, and

Flt concentrations were significant and negative. The TSP concentrations before cigarettes had been smoked ranged from 8.4 to 33.5 $\mu g/m^3$, and the median was 20.9 $\mu g/m^3$. The correlations between the TSP, particulate-phase PAH, and gas-phase PAH concentrations before cigarettes had been smoked were not statistically significant.

The correlation coefficients for the relationships between the concentrations of the different PAHs in the particulate-phase and gas-phase air samples collected after cigarettes had been smoked were also calculated. Many of these correlation coefficients were significant.

The correlation coefficients for the relationships between the concentrations of the PAHs in the particulate-phase samples collected after cigarettes had been smoked are summarized in Table 6. The PAHs listed were detected in eight or more of the 16 air samples. The correlation coefficients for the relationships between the BaA, Chr, BbF, BkF, and BaP concentrations were>0.74 ($p<0.001$), and the correlation coefficients for the relationships between the Nap and Ace concentrations and the BaA, Chr, BbF, and BkF concentrations were 0.70-0.95 ($p<0.001$). The correlations between the Nap concentrations and many of the four- and five-ring PAH concentrations were significant and positive. The correlation coefficients for the relationships between the BaP, IP, DahA, and BP concentrations were also relatively high (e.g., the correlation coefficients for the relationships between the BaP and IP concentrations and between the IP and BP concentrations were 0.82 and 0.72, respectively). One particulate PAH precursor affects the production of particulate PAH group 1 (Nap, BaA, Chr, BbF, BkF, and BaP), and another precursor affects the production of particulate BaP and particulate PAH group 2 (IP, DahA, and BP).

The correlation coefficients for the relationships between the PAH concentrations in the gas-phase air samples collected after cigarettes had been smoked are shown in Table 7. The correlation coefficients for the relationships between the Nap, Acy, Ace, and Flu concentrations were>0.82 ($p<0.001$), and the correlation coefficients for the relationships between the Phe, Ant, Flt, Pyr, and BaA concentrations were 0.68-0.97. The correlations between the two- to four-ring PAH concentrations were significant and positive. The TSP concentrations after cigarettes had been smoked were 73-152 $\mu g/m^3$, and the median was 105 $\mu g/m^3$. The relationship between the TSP concentration and the sum of the particulate-phase concentrations of six PAHs (Nap+BaA+Chr+BbF+BkF+BaP) after cigarettes had been smoked are shown in Fig. 1.

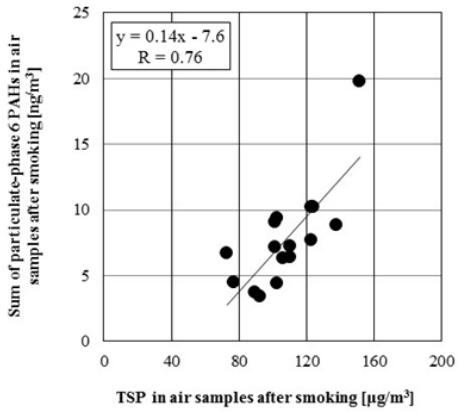

Fig. 1 Relationship between the TSP concentration and the total of the particulate-phase concentrations of six PAHs (Nap + BaA + Chr + BbF + BkF + BaP) after smoking

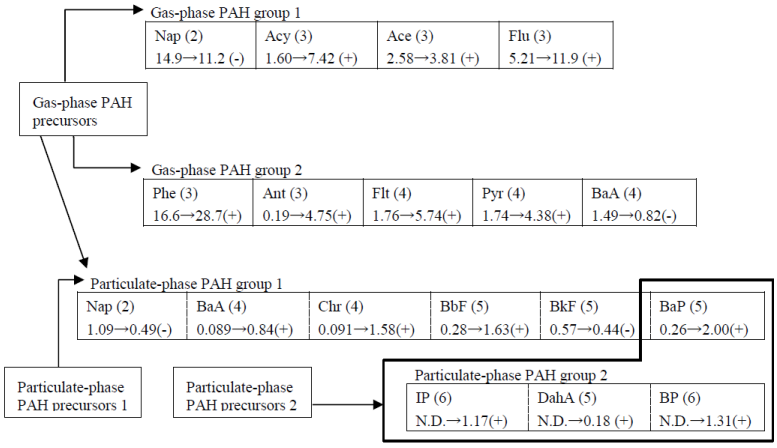

Fig. 2 Formation pass for some PAHs. The upper lines show the abbreviation of PAHs (the number of ring) and the lower lines show the concentrations before smoking→the concentrations after smoking (+means that the concentrations after smoking were higher). The PAH abbreviations are shown in the introduction and section 2.2.

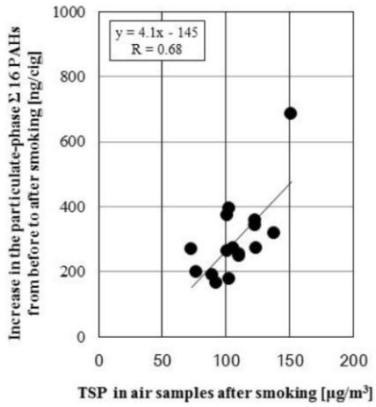

Fig. 3 Relationship between TSP and increase in the total particulate-phase Σ16 PAHs

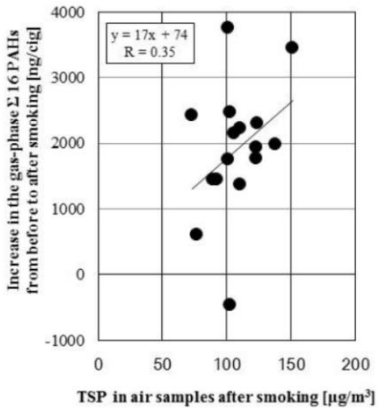

Fig. 4 Relationship between TSP and increase in the total gas-phase Σ16 PAHs

The correlation coefficient for the relationship was 0.76 ($p<0.001$). This may indicate that the formation of TSP was associated with the formation of these six PAHs when cigarettes were smoked. The correlation between the TSP concentration and the sum of the gas-phase concentrations of five PAHs (Phe+Ant+Flt+Pyr+BaA) was not significant, but the correlation coefficient for the relationship between the sum of the particulate-phase concentrations of the six PAHs and the sum of the gas-phase concentrations of the five PAHs was 0.72 ($p<0.001$).

The routes through which some of PAHs may have formed are shown in Fig. 2. The correlation coefficients for the relationships between the gas-phase concentrations of the group 1 PAHs before and after cigarettes had been smoked were high, and the gas-phase concentrations of the PAHs except Nap were higher after than before cigarettes had been smoked. The correlation coefficients for the relationships between the gas-phase concentrations of the group 2 PAHs after cigarettes had been smoked were high, and the concentrations of the PAHs except for BaA were higher after than before cigarettes had been smoked. The correlations between the gas-phase concentrations of the group 1 and group 2 PAHs were significant and positive. The results indicate that gas-phase PAHs are probably formed from similar precursors. The gas-phase Nap and BaA concentrations may have been lower after than before cigarettes had been smoked because the PAHs were decomposed and transformed into different chemicals when the cigarettes were smoked.

The correlation coefficients for the relationships between the concentrations of some of the particulate-phase group 1 PAHs before and after cigarettes had been smoked were high, and the correlation coefficients for the relationships between the concentrations of the other PAHs before and after cigarettes had been smoked were high. The particulate-phase concentrations of Nap and BkF were lower after than before cigarettes had been smoked, but the particulate-phase concentrations of the other PAHs were higher after than before cigarettes had been smoked. This may have been because particulate-phase Nap and BkF decomposed and were transformed into different chemicals while cigarettes were smoked. The correlation coefficients for the relationships between the particulate-phase concentration of BaP (in group 1) and the particulate-phase concentrations of group 2 PAHs after cigarettes had been smoked were high. These results probably indicate that particulate-phase group 1 PAHs are formed from one of the particulate-phase PAH precursors and that particulate-phase BaP and group 2 PAHs are formed from different precursors. The correlation coefficients for the relationships between the gas-phase group 1 and 2 PAH concentrations and the particulate-phase group 1 PAH concentrations were high, so the gas-phase PAH precursors probably affect the production of particulate-phase group 1 PAHs.

The increases in the total particulate-phase and gas-phase concentrations of the 16 PAHs per cigarette smoked were defined as the differences in the concentrations found after cigarettes had been smoked multiplied by 66 m^3 subtracted from the concentrations found before cigarettes had been smoked multiplied by 24 m^3 and then divided by two (because two cigarettes were smoked in each experiment). The increases in the total particulate-phase concentrations of the 16 PAHs per cigarette ranged from 165 to 683 ng, and the median was 271 ng. The increases in the total gas-phase concentrations of the 16 PAHs per cigarette ranged from −476 to 3750 ng, and the median was 1960 ng. The relationships between the TSP concentration and the increase in the total particulate-phase concentration of the 16 PAHs per cigarette and between the TSP concentration and the increase in the total gas-phase concentration of the 16 PAHs per cigarette are shown in Figs. 3 and 4, respectively. A significant positive correlation was found between the TSP concentration and the increase in the total particulate-phase concentration of the 16 PAHs, and the increase in the total gas-phase concentration of the 16 PAHs tended to increase as the TSP concentration increased. This probably indicates that decreasing the amount of TSP produced will

lead to smaller amounts of PAHs being produced.

4. Conclusions

The concentrations of PAHs released by smoked cigarettes were studied. Four brands of cigarettes with tar contents of 6-19 mg/cigarette were used. The concentrations of 16 PAHs in air samples collected before and after cigarettes were smoked were measured.

In the air samples collected before cigarettes had been smoked, 15 PAHs were found in the particulate-phase samples and 15 in the gas-phase samples. The total particulate-phase PAH concentrations ranged from 1.35 to 13.2 ng/m^3, and the median was 3.13 ng/m^3. The total gas-phase PAH concentrations ranged from 29.4 to 166 ng/m^3, and the median was 48.0 ng/m^3. The most abundant PAHs in the particulate phase and gas phase were Nap and Phe, respectively.

In the air samples collected after cigarettes had been smoked, 14 PAHs were found in the particulate-phase samples and 16 in the gas-phase samples. The total particulate-phase PAH concentrations ranged from 5.71 to 23.4 ng/m^3, and the median was 10.0 ng/m^3. The total gas-phase PAH concentrations ranged from 35.5 to 128 ng/m^3, and the median was 79.6 ng/m^3. The most abundant PAHs in the particulate phase and gas phase were BaP and Phe, respectively. Both before and after cigarettes had been smoked, the gas-phase PAH concentrations were much higher than the particulate-phase PAH concentrations. The particulate-phase and gas-phase PAH concentrations were higher after than before cigarettes had been smoked.

The correlation coefficients for the relationships between the particulate-phase and gas-phase PAH concentrations in the air samples collected before and after cigarettes had been smoked were calculated. The two- to four-ring gas-phase PAHs (Nap, Acy, Ace, Flu, Phe, Ant, Flt, Pyr, and BaA) were probably formed from similar precursors. Particulate-phase Nap and the higher molecular weight particulate-phase PAHs (BaA, Chr, BbF, BkF, and BaP) were probably formed from similar precursors. For the particulate-phase PAHs, the formation of BaP was found to be related to the formation of IP, DahA, and BP. The two- to four-ring gas-phase PAHs appeared to affect the formation of the higher molecular weight particulate-phase PAHs.

The median increases in the total concentrations of the 16 PAHs per cigarette were 271 ng for the particulate-phase PAHs and 1960 ng for the gas-phase PAHs. The increases in the particulate-phase and gas-phase concentrations of the 16 PAHs tended to increase as the TSP concentration increased. Further studies will be required, but we conclude that decreasing the amount of TSP produced may effectively inhibit the production of PAHs while cigarettes are smoked.

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