Determination of Polycyclic Aromatic Hydrocarbons in Cigarettes and Cigarette Smoke

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Received: July 7, 2016Accepted: August 5, 2016Online Published: September 29, 2016doi:10.5539/ep.v5n2p15URL: http://dx.doi.org/10.5539/ep.v5n2p15

Abstract

The present study examines the concentrations of polycyclic aromatic hydrocarbons (PAHs) in cigarettes and sidestream cigarette smoke. Nine PAHs were determined in sidestream cigarette smokes for five types of cigarettes. The volume of the experimental room is approximately 66 m³. The air samples in the room were collected before and after smoking. The total PAH concentrations were approximately 1.0 ng/m³ before smoking, but the median concentration and the range of PAHs were 29.1 ng/m³ and from 7.62 to 57.6 ng/m³ after smoking. The relationship between suspended particulate matter (SPM) and total PAHs after smoking is significant and proportional. This may indicate that the SPM formation is associated with PAH formation during smoking. Furthermore, nine PAHs were determined in the cigarettes. Median PAH contents in the five brands of cigarettes ranged from 221 to 936 ng per cigarette before smoking and from 66.9 to 266 ng per cigarette after smoking. Mean PAH emissions from cigarettes while smoking ranged from 257 to 1490 ng per cigarette. The results show that PAHs in the cigarettes, and those generated during smoking, were emitted into the air.

Keywords: cigarette, polycyclic aromatic hydrocarbons, sidestream cigarette smoke, suspended particulate matter

1. Introduction

Exposure to cigarette smoke creates significant risks for developing cancers and a variety of respiratory and cardiovascular diseases (OEHHA 2005). Smoking has been recognized as a major cause of lung cancer (Lee et al. 2001; IARC 2004). Many studies have also provided evidence that smoking is a major cause of heart disease (Villablanca et al. 2000; Messner et al. 2014). Cigarette smoke has a complex chemical composition and contains numerous toxic chemicals and carcinogens, including polycyclic aromatic hydrocarbons (PAHs) (IARC 1987, 2010). PAHs have been measured in various environments because they are produced primarily as a result of incomplete combustion from anthropogenic sources such as cars, incinerators, and factories (Liu et al. 2015; Nam et al. 2008; Obrist et al. 2015; Subramanian et al. 2015). Benzo[a]pyrene is a PAH that has been classified as a Group 1 carcinogen (carcinogenic to humans) by the International Agency for Research on Cancer (IARC) (IARC 2016). Dibenz[a,h]anthracene, dibenz[a,j]acridine, dibenzo[a,l]pyrene have been classified as Group 2A carcinogens (probably carcinogenic to humans). Thirteen PAHs have been classified as Group 2B carcinogens (possibly carcinogenic to humans). Many PAHs, including benzo[a]pyrene and benzo[b]fluoranthene, are also considered to be mutagenic (Luch 2005). Because of their adverse effects some countries have regulated PAHs. For example, the United States Environmental Protection Agency has designated many PAHs in the Toxic Pollutant List and Priority Pollutant List under the Clean Water Act (USEPA 2016). Anthracene is included in the European Commission's REACH Candidate List (ECHA 2016).

Some experimental studies have reported PAHs in cigarette smoke (Ding et al. 2007; Lee et.al 2011; Vu et al. 2015). PAHs have been detected in some smokeless tobacco containing fire-cured tobacco varieties (Stepanov et al. 2010; McAdam et al. 2013). This is because when tobacco is fire-cured, PAHs formed by smoldering wood are absorbed in the tobacco leaves (Bentley et al. 1960). To understand PAH emissions from cigarettes and their formation during smoking, this study examined the occurrence of PAHs in cigarettes (leaves and filters) and sidestream cigarette smoke (particulate).

2. Materials and Methods

2.1 Samples

Five brands of cigarettes were investigated in this study. The tar and nicotine contents per cigarette ranged from 1 to 21 mg and from 0.1 to 1.9 mg, respectively. PAH in air samples and cigarette samples before and after smoking were measured as shown in Table 1.

The numbers of air samples collected for Brands A–D and Brand E before and after smoking were 5 and 4, respectively. The air sampling room was 2.5 m high, 5.3 m in length, and 5.0 m in width (approximately 66 m³). The air samples were collected at a rate of 400 L/min for 2.0 h (48 m³) using a high-volume air sampler (HV-500R; Sibata Scientific Technology Ltd., Souka, Japan) before the cigarettes were smoked. A quartz fiber filter (QR-100; Advantec, Tokyo, Japan) was used in the sampler. The filter had a minimum particle collection efficiency of 99.99% for particles 0.3 μ m in diameter when air passed through the sampler at a speed of 5 cm/s. After the initial air sampling, two cigarettes were smoked in the experimental room. The sidestream smoke samples were collected at a rate of 400 L/min for 2.75 h (66 m³). Particulate PAHs collected on the quartz fiber filters were analyzed as discussed in the Analytical methods and instruments section.

PAHs in cigarettes before and after smoking were also analyzed. The numbers of cigarette samples (before smoking) and cigarette butt samples (after smoking) for Brands A–E were 4 and 1, respectively. The filter and leaf weights per cigarette are shown in Table 2. The arithmetic means of the weights of the five brands of cigarettes before smoking (n = 4) ranged from 0.19 to 0.25 g for the filters and from 0.54 to 0.72 g for the leaves. The weights in the five brands of cigarettes after smoking (n = 1) ranged from 0.19 to 0.27 g for the filters and from 0.09 to 0.12 g for the leaves. Filters and leaves of the cigarettes were cut into three and six parts (Fig. 1), respectively. A portion of the filters and two portions of the leaves in the cigarette samples were analyzed as discussed in the Analytical methods and instruments section. After each of five brands of cigarettes were smoked, whole filters and leaves of the cigarette butt samples were also analyzed.

	Air sample		Cigarette sample		Cigarette butt sample	
	Before	After	(before	smoking)	(after sn	noking)
_	smoking	smoking	Filter	Leaf	Filter	Leaf
Brand A	5	5	4	8(4×2)	1	1
Brand B	5	5	4	8(4×2)	1	1
Brand C	5	5	4	8(4×2)	1	1
Brand D	5	5	4	8(4×2)	1	1
Brand E	4	4	4	8(4×2)	1	1
Total	24	24	20	40(20×2)	5	5

Table 1. Numbers of air and cigarette samples in this study

Note. Two portions of cigarette leaves for cigarette sample were analyzed.

Table 2. Cigarette weights before and after smoking

	Cigarette	sample	Cigarette b	utt sample
	(before s	(before smoking) Filter Leaf		noking)
	Filter			Leaf
Brand A	0.24	0.54	0.25	0.09
Brand B	0.25	0.58	0.25	0.11
Brand C	0.25	0.58	0.25	0.09
Brand D	0.24	0.67	0.27	0.12
Brand E	0.19	0.72	0.19	0.12

Note. The weights for cigarette sample are the arithmetic means (n = 4) and those for cigarette butt sample are the measured values (n = 1). All units are g.



Figure 1. Analyzed portions of cigarette sample

2.2 PAHs

The nine PAHs shown in Table 3 were the target compounds in this study because many studies have reported that they are frequently detected in smoking environments. Some PAHs, for example BaA, BaP, BbF, BkF, DahA, FL and PY, are designated as hazardous substances that have the potential to harm humans through long-term exposure under Japanese air pollution control laws.

Nine standard material grade PAHs were purchased from Wako Pure Chemical Industries, Ltd. and were diluted with acetone and hexane to produce calibration standards.

2.3 Analytical Methods and Instruments

The quartz fiber filters were weighed using an electronic balance before and after smoking. The filters after smoking were cut into 16 portions. All portions were placed into 260 mL bottles and extracted with 40 mL of dichloromethane for 15 min by ultrasonic cleaner. The extract was concentrated to 2 mL using a rotary evaporator and was filtered using a disposable filter device (PURADISCTM 25TF; Whatman, Buckinghamshire, UK). The extract was then concentrated to 0.1 mL under N_2 flow. Finally, hexane was added to the extract to produce a final volume of 2 mL.

Filters and leaves of the cigarettes before and after smoking were analyzed. Each sample was weighed, placed into a cellulose extraction thimble, and extracted with 40 mL of dichloromethane for 15 min by ultrasonic cleaner. The extract was concentrated to 2 mL using a rotary evaporator. The extract was filtered using a disposable filter device and concentrated to 0.1 mL under N_2 flow. Hexane was then added to the extract to produce a final volume of 2 mL.

Table 3.	PAHs	measured	in	this	study
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PAHs	CAS No.	Abbreviation	Detection limits [pg]
Anthracene	120-12-7	AN	4.0
Benzo[a]anthracene	56-55-3	BaA	11.7
Benzo[b]fluoranthene	205-99-2	BbF	9.2
Benzo[k]fluoranthene	207-08-9	BkF	10.7
Benzo[ghi]perylene	191-24-2	BghiP	22.6
Benzo[a]pyrene	50-32-8	BaP	11.4
Dibenz[a,h]anthracene	53-70-3	DahA	22.9
Fluoranthene	206-44-0	FL	2.6
Pyrene	129-00-0	PY	2.4

Note. The abbreviations are used in this study. The detection limits were calculated as three times the signal-to-noise ratio at the baseline of the chromatogram.

The PAH concentrations in the extracts were determined using gas chromatography-mass spectrometry (5975B inert XL E/CI MSD; Agilent Technologies, Santa Clara, CA, USA) equipped with a HP-5MS capillary column ($30m \times 0.25 \text{ mm}$ i.d., $0.25\mu \text{m}$ film thickness; Agilent Technologies). The GC conditions were as follows: splitless injection of 2 μ L; injection port temperature of 250°C; GC temperature program; 70 °C (hold 1.5 min) to 180 °C at 20 °C/min, and to 280 °C at 5 °C/min (hold 1 min); and the carrier gas was helium. The mass spectrometer was operated in the electron impact mode with an electron energy of 70 eV. After each pollutant was identified using three representative fragment ions, it was quantified using the largest one. Quantification was performed using an external calibration method. The recoveries and the variation coefficients of the measured PAHs ranged from 75 to 110 % and from 7 to 15%, respectively.

Suspended particulate matter concentrations were calculated as the differences between the weights of the quartz fiber filters before and after air sampling divided by 48 m^3 (before smoking) or 66 m^3 (after smoking).

3. Results and Discussion

3.1 PAHs in Air Samples

Seven PAHs were detected in the air samples before smoking the cigarettes. Fluoranthene (FL) and pyrene (PY) were detected in almost all of the 24 samples. The median and maximum concentrations of FL were 0.46 ng/m³ and 1.30 ng/m³, respectively. The median and maximum concentrations for sum total of all PAHs were 1.06 ng/m³ and 5.27 ng/m³.

Nine PAHs, as shown in Table 4, were detected in the air samples after smoking the cigarettes. Benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[ghi]perylene (BghiP), FL and PY were detected in all 24 samples. The median concentration of BaP, which was the most abundant PAH, was 7.89 ng/m³ and its concentrations ranged from 2.50 to 14.6 ng/m³. Using BaP as an indicator of general PAH mixtures from emissions of coke ovens and similar combustion processes in urban air, and a reported value of 0.71% BaP in the benzene-soluble fraction of coke oven emissions, the unit risk for BaP as an indicator air constituent for PAHs was estimated to be 8.7×10^{-5} per ng/m³ (WHO 1987). The lifetime respiratory cancer risk of the median concentrations ranged from 7.62 to 57.6 ng/m³. The mean mole ratios for the PAHs were; 28.0 % for BaP, 21.1 % for BaA, 18.3 % for BbF and BghiP, 4.6 % for FL, 3.3 % for dibenz[a,h]anthracene (DahA), 3.1 % for anthracene (AN), 2.7 % for PY, and 0.6 % for benzo[k]fluoranthene (BkF), respectively.

The correlation coefficients among the detected PAHs in air samples after smoking are summarized in Table 5. The correlation coefficients between AN and other PAHs were not significant because AN can play an important role as a precursor to higher PAHs (Kislov et al. 2013). However, the correlation coefficients for almost all of the other detected PAHs were greater than 0.643 (p < 0.01), showing that each PAH was strongly related to the other PAHs. This is probably because the measured PAHs are formed through similar precursors (Richter et al. 1999, 2000, Vu et.al 2015).

The median concentration of suspended particulate matter (SPM) before smoking was 17 μ g/m³ and the SPM concentrations ranged from 8 to 30 μ g/m³. After smoking, the median SPM concentration was 117 μ g/m³ and concentrations ranged from 96 to 146 μ g/m³. The relationship between SPM concentrations and total PAH concentrations after smoking is presented in Fig. 2. The correlation coefficient was 0.559 (p < 0.01). This may indicate that SPM formation is associated with PAH formation during smoking.

	Brand A	Brand B	Brand C	Brand D	Brand E
AN	0.67 (3/5)	0.47 (4/5)	0.64 (5/5)	0.24 (3/5)	N.D. (1/4)
AN	[N.D. – 1.06]	[N.D. – 1.41]	[0.41 - 0.97]	[N.D. – 1.33]	[N.D. – 0.41]
DeA	4.93 (5/5)	8.86 (5/5)	7.37 (5/5)	1.13 (5/5)	11.1 (4/4)
BaA	[4.39 - 5.92]	[5.54 - 10.1]	[5.43 - 8.34]	[0.89 - 1.27]	[6.14 - 12.0]
DLE	6.71 (5/5)	7.24 (5/5)	4.26 (5/5)	1.63 (5/5)	9.00 (4/4)
BOL	[5.00 - 7.85]	[6.12 - 8.10]	[3.75 – 4.61]	[1.44 – 1.75]	[7.30 – 11.7]
DI-E	N.D. (1/5)	N.D. (1/5)	N.D. (0/5)	N.D. (0/5)	N.D. (1/4)
BKF	[N.D. – 1.43]	[N.D. – 1.82]	[N.D.]	[N.D.]	[N.D 2.03]
DahiD	7.47 (5/5)	9.02 (5/5)	3.88 (5/5)	1.80 (5/5)	12.0 (4/4)
БдшР	[4.40 - 9.28]	[7.64 – 9.80]	[3.05 - 4.19]	[1.14 – 1.94]	[10.2 - 12.9]
DoD	7.88 (5/5)	11.5 (5/5)	7.44 (5/5)	2.97 (5/5)	12.8 (4/4)
Dar	[7.22 - 9.10]	[9.19-12.4]	[5.93 - 8.38]	[2.50 - 3.20]	[10.1 - 14.6]
Dah A	N.D. (0/5)	3.53 (4/5)	1.36 (4/5)	0.45 (4/5)	N.D. (1/4)
DanA	[N.D.]	[N.D 4.42]	[N.D. – 2.25]	[N.D. – 0.51]	[N.D. – 4.11]
EI	1.48 (5/5)	1.43 (5/5)	1.00 (5/5)	0.31 (5/5)	1.45 (4/4)
ГL	[1.05 - 1.90]	[1.03 – 1.89]	[0.74 - 1.02]	[0.27 - 0.34]	[1.26 - 1.70]
DV	0.96 (5/5)	0.83 (5/5)	0.54 (5/5)	0.18 (5/5)	0.86 (4/4)
Ρĭ	[0.64 - 1.25]	[0.64 - 1.34]	[0.43 - 0.64]	[0.12 - 0.20]	[0.37 - 1.06]
NODALL	30.0 (5/5)	43.0 (5/5)	26.3 (5/5)	8.85 (5/5)	47.6 (4/4)
Σ9PAHs	[25.4 - 34.9]	[32.2 - 48.6]	[21.2 - 28.2]	[7.62 – 9.01]	[37.4 – 57.6]

Table 4. PAHs in air samples after smoking

Note. The upper values show median concentration (detection rate) and the lower values show [concentration range]. All units are ng/m^3 . N.D. means Not detected. Σ 9PAHs means total PAH concentrations.

Table 5. Pearson Coefficients for Correlations among the detected PAHs in air samples after smoking

_		AN	BaA	BbF	BkF	BghiP	BaP	DahA	FL
_	BaA	-0.268							
	BbF	-0.062	0.861*						
	BkF	-	0.993	0.898					
	BghiP	-0.153	0.804*	0.939*	0.991				
	BaP	-0.164	0.943*	0.952*	0.951	0.922*			
	DahA	0.021	0.888*	0.936*	-	0.960*	0.950*		
	FL	0.123	0.723*	0.890*	-0.975	0.774*	0.828*	0.935*	
	PY	0.074	0.643*	0.803*	-0.869	0.710*	0.722*	0.905*	0.913*

Note. *; p < 0.01.



Figure 2. Relationship between SPM and total PAHs in air samples after smoking

3.2 PAHs in Cigarettes

PAHs in the cigarette filters before and after smoking are shown in Table 6 and Table 7, respectively. Five PAHs were detected in the cigarette filters before smoking. FL was detected in almost every samples. The median concentration of BbF, which was the most abundant PAH, was 87.9 ng/g and BbF concentrations ranged from N.D. to 139 ng/g. The median total PAH concentration was 155 ng/g and total PAH concentrations ranged from N.D. to 460 ng/g. Five PAHs were detected in the cigarette filters after smoking. The median total PAH concentrations ranged from N.D. to 355 ng/g. The PAHs were detected in the cigarette filters after smoking. The PAH concentrations in cigarette filters tended to be a little higher before smoking than after smoking. It may indicate that the PAHs produce during the cigarette production process and stay in the filters.

PAHs in the cigarette leaves before and after smoking are shown in Table 8 and Table 9, respectively. Nine PAHs were detected in the cigarette leaves before smoking. FL and PY were detected in all 40 samples. The median concentration of BaA, the most abundant PAH, was 257 ng/g and its concentrations ranged from N.D. to 441 ng/g. The median total PAH concentration was 750 ng/g and concentrations ranged from 206 to 2400 ng/g. Six PAHs were detected in the cigarette leaves after smoking. AN, BaA, FL and PY were detected in all five samples. The median total PAH concentration was 1030 ng/g and total concentrations ranged from 744 to 1710 ng/g. The PAH concentrations in cigarette leaves were greater after smoking than before smoking. The total concentrations of PAHs were higher in cigarette leaves than in cigarette filters.

	Brand A	Brand B	Brand C	Brand D	Brand E
AN	79.9 (4/4)	N.D. (0/4)	N.D. (0/4)	23.7 (2/4)	76.7 (3/4)
AIN	[31.9-324]	[N.D.]	[N.D.]	[N.D. – 195]	[N.D. – 118]
Dat	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)
BaA	[N.D.]	[N.D.]	[N.D.]	[N.D.]	[N.D.]
DFE	N.D. (1/4)	N.D. (1/4)	83.6 (4/4)	N.D. (0/4)	N.D. (1/4)
БОГ	[N.D. – 139]	[N.D 68.9]	[69.6 – 118]	[N.D.]	[N.D. – 117]
DLE	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)	N.D. (1/4)	N.D. (0/4)
DKF	[N.D.]	[N.D.]	[N.D.]	[N.D. – 26.5]	[N.D.]
DahiD	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)
DgillF	[N.D.]	[N.D.]	[N.D.]	[N.D.]	[N.D.]
BaD	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)
Dal	[N.D.]	[N.D.]	[N.D.]	[N.D.]	[N.D.]
DobA	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)	N.D. (0/4)
DallA	[N.D.]	[N.D.]	[N.D.]	[N.D.]	[N.D.]
EI	37.8 (3/4)	49.3 (3/4)	52.3 (4/4)	52.4 (4/4)	64.9 (3/4)
ГL	[N.D. – 84.1]	[N.D 71.0]	[42.3 – 166]	[20.6 - 90.0]	[N.D. – 98.9]
ΡV	19.6 (2/4)	30.6 (3/4)	40.9 (4/4)	38.0 (3/4)	29.2 (2/4)
I I	[N.D. – 52.4]	[N.D 42.0]	[25.2 - 110]	[N.D. – 56.1]	[N.D 63.0]
ΣΟΡΑ Η α	196 (4/4)	79.9 (3/4)	171 (4/4)	122 (4/4)	169 (4/4)
29PAHs	[53.3 - 460]	[N.D. – 182]	[149 – 394]	[20.6 - 353]	[83.2-318]

Table 6. PAHs in cigarette filters before smoking

Note. The upper values show median concentration (detection rate) and the lower values show [concentration range]. All units are ng/g. N.D. means Not detected. Σ 9PAHs means total PAH concentrations.

Table 7. PAHs in cigarette filters after smoking

	Brand A	Brand B	Brand C	Brand D	Brand E
AN	N.D. (0/1)	N.D. (0/1)	N.D. (0/1)	N.D. (0/1)	101 (1/1)
BaA	N.D. (0/1)	N.D. (0/1)	N.D. (0/1)	42.4 (1/1)	N.D. (0/1)
BbF	56.6 (1/1)	N.D. (0/1)	N.D. (0/1)	N.D. (0/1)	N.D. (0/1)
BkF	N.D. (0/1)				
BghiP	N.D. (0/1)				
BaP	N.D. (0/1)				
DahA	N.D. (0/1)				
FL	30.2 (1/1)	N.D. (0/1)	9.6 (1/1)	26.7 (1/1)	135 (1/1)
PY	26.2 (1/1)	N.D. (0/1)	N.D. (0/1)	22.9 (1/1)	119 (1/1)
Σ9PAHs	113 (1/1)	N.D. (0/1)	9.6 (1/1)	92.0 (1/1)	355 (1/1)

Note. The values show median concentration (detection rate). All units are ng/g. N.D. means Not detected. Σ 9PAHs means total PAH concentrations.

	Brand A	Brand B	Brand C	Brand D	Brand E
A NI	53.7 (8/8)	N.D. (0/8)	N.D. (2/8)	N.D. (3/8)	69.9 (6/8)
AN	[39.4 - 502]	[N.D.]	[N.D. – 205]	[N.D. – 24.9]	[N.D. – 86.4]
BaA	N.D. (1/8)	N.D. (0/8)	N.D. (2/8)	169 (7/8)	341 (6/8)
	[N.D 239]	[N.D.]	[N.D. – 232]	[N.D. – 319]	[N.D. – 441]
DhE	101 (5/8)	N.D. (2/8)	47.3 (7/8)	N.D. (3/8)	97.8 (7/8)
БОГ	[N.D. – 356]	[N.D. – 41.7]	[N.D. – 82.9]	[N.D. – 199]	[N.D. – 119]
DLE	N.D. (2/8)	N.D. (0/8)	N.D. (0/8)	53.7 (7/8)	N.D. (0/8)
DKΓ	[N.D 376]	[N.D.]	[N.D.]	[N.D. – 195]	[N.D.]
DahiD	N.D. (0/8)	N.D. (0/8)	N.D. (0/8)	N.D. (1/8)	N.D. (0/8)
БgшР	[N.D.]	[N.D.]	[N.D.]	[N.D. – 75.5]	[N.D.]
DoD	58.9 (4/8)	N.D. (0/8)	N.D. (3/8)	68.4 (6/8)	89.0 (6/8)
Dar	[N.D 424]	[N.D.]	[N.D. – 82.2]	[N.D 230]	[N.D. – 122]
DohA	N.D. (2/8)	N.D. (0/8)	N.D. (0/8)	N.D. (2/8)	N.D. (0/8)
DallA	[N.D 483]	[N.D.]	[N.D.]	[N.D. – 174]	[N.D.]
EI	304 (8/8)	195 (8/8)	221 (8/8)	162 (8/8)	387 (8/8)
ГL	[276 - 402]	[119 – 263]	[145 - 354]	[113 - 210]	[304 - 547]
DV	265 (8/8)	120 (8/8)	124 (8/8)	134 (8/8)	359 (8/8)
Γĭ	[246 - 345]	[86.2 – 179]	[86.9 - 233]	[94.0-178]	[275 - 505]
	863 (8/8)	346 (8/8)	391 (8/8)	630 (8/8)	1260 (8/8)
Σ9PAHs	[608 - 2400]	[206 - 442]	[270 - 1090]	[238 - 1560]	[775 – 1570]

Table 8. PAHs in cigarette leaves before smoking

Note. The upper values show median concentration (detection rate) and the lower values show [concentration range]. All units are ng/g. N.D. means Not detected. Σ 9PAHs means total PAH concentrations.

Table 9. PAHs in cigarette leaves after smoking

	Brand A	Brand B	Brand C	Brand D	Brand E
AN	86.8 (1/1)	64.6 (1/1)	69.2 (1/1)	167 (1/1)	117 (1/1)
BaA	334 (1/1)	215 (1/1)	333 (1/1)	394 (1/1)	382 (1/1)
BbF	N.D. (0/1)	N.D. (0/1)	N.D. (0/1)	111 (1/1)	129 (1/1)
BkF	N.D. (0/1)				
BghiP	N.D. (0/1)				
BaP	N.D. (0/1)	N.D. (0/1)	N.D. (0/1)	154 (1/1)	164 (1/1)
DahA	N.D. (0/1)				
FL	336 (1/1)	270 (1/1)	365 (1/1)	501 (1/1)	468 (1/1)
PY	253 (1/1)	195 (1/1)	264 (1/1)	386 (1/1)	398 (1/1)
Σ9PAHs	1010 (1/1)	744 (1/1)	1030 (1/1)	1710 (1/1)	1660 (1/1)

Note. The values show median concentration (detection rate). All units are ng/g. N.D. means Not detected. Σ 9PAHs means total PAH concentrations.

3.3 PAH Formation during Smoking

The median contents for the nine PAHs in the five types of cigarettes before and after smoking are presented in Fig. 3. The median contents were calculated as the median concentrations for the nine PAHs in Tables 6–9 multiplied by the weights in Table 2. Median contents before smoking ranged from 20.0 to 47.0 ng per cigarette

for the filters and from 201 to 904 ng per cigarette for the leaves. Those after smoking ranged from N.D. to 67.5 ng per cigarette for the filters and from 66.9 to 206 ng per cigarette for the leaves. The PAH contents in the filters before and after smoking were approximately equal. However, those for the leaves were higher before smoking than after smoking. PAH emissions per cigarette were calculated as the difference between concentrations before and after smoking multiplied by 66 m³ and then divided by two because two cigarettes were smoked in the air sampling room (approximately 66 m³) during the experiments. The arithmetic means \pm standard errors (range) of the PAH emissions per cigarette were 899 \pm 62 ng for Brand A, 1330 \pm 170 ng for Brand B, 781 \pm 88 ng for Brand C, 257 \pm 36 ng for Brand D, and 1490 \pm 196 ng for Brand E. Fourteen PAHs in mainstream smoke particulate matter from 28 brands of cigarettes in many counties have been reported (Ding et al. 2007). The mean emissions in this study, for which high molecular PAHs dominated emissions, ranged from 257 to 1490 ng per cigarette and, which was higher than the emissions reported by Ding et al. PAHs in sidestream smoke are likely to be more concerning than those in mainstream smoke. The results of this study show that cigarettes contain PAHs, especially in the cigarette leaves. It was also clear that PAHs in the cigarettes and PAHs generated during smoking are emitted into the air.



Figure 3. Comparison of median contents of total PAHs in cigarettes for Brands A-E

Note. Before indicates before smoking, and After indicates after smoking. Solid bars and open bars show contents for leaves and filters, respectively.

4. Conclusion

Nine PAHs in five types of cigarettes and the PAH emissions from cigarettes and their formation during smoking were investigated. PAHs were determined in air samples before and after two cigarettes were smoked in the air sampling room (approximately 66 m³). The total PAH concentrations were approximately 1.0 ng/m³ before smoking and ranged from 7.62 to 57.6 ng/m³ after smoking. Except for anthracene, the correlation coefficients between the detected PAHs in air samples after smoking were significantly positive. This is probably because the detected PAHs are formed from similar precursors. The correlation coefficient between SPM and the total concentration of the nine PAHs after smoking was also significantly positive. This may indicate that SPM formation is associated with PAH formation while smoking.

PAHs in the cigarettes before and after smoking were also measured. The total concentrations of the PAHs in the cigarette filters ranged from N.D. to 460 ng/g before smoking, and from N.D. to 355 ng/g after smoking. Those in the cigarette leaves ranged from 206 to 2400 ng/g before smoking, and from 744 to 1710 ng/g after smoking. Median PAH contents in the five brands of cigarettes before smoking ranged from 20.0 to 47.0 ng per cigarette for the filters and from 201 to 904 ng per cigarette for the leaves. Those after smoking ranged from N.D. to 67.5

ng per cigarette for the filters and from 66.9 to 206 ng per cigarette for the leaves. Mean PAH emissions from the cigarettes to the air while smoking ranged from 257 to 1490 ng per cigarette. The results show that PAHs in the cigarettes, and those generated during smoking, were emitted into the air.

Acknowledgments

The author would like to thank Kindai University for providing the grant to complete this research. The author acknowledge the assistance given by Hajime Kaku and Takahiro Fujiwara.

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