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Seasonal Trends of Atmospheric PAHs in Five Asian Megacities and Source Detection Using Suitable Biomarkers

Mahua Saha[1], Dusmant Maharana[1], Rina Kurumisawa[2], Hideshige Takada[2*], Bee Geok Yeo[2], Andrea C. Rodrigues[1], Badal Bhattacharya[3], Hidetoshi Kumata[4], Tomoaki Okuda[5], Kebin He[6], Yongliang Ma[6], Fumiyuki Nakajima[7], Mohamad Pauzi Zakaria[8], Duong Hoang Giang[9], Pham Hung Viet[9]

[1] *Chemical Oceanography Division, CSIR-National Institute of Oceanography, Dona Paula, Goa 403004, India*
[2] *Laboratory of Organic Geochemistry, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 1838509, Japan*
[3] *Institute of Ecotoxicology and Environmental Sciences, Salt Lake, Kolkata 700097, West Bengal, India*
[4] *Tokyo University of Pharmacy and Life Sciences, Hachioji, Tokyo 1920392, Japan*
[5] *Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Kohoku-ku, Yokohama 2238522, Japan*
[6] *School of Environment, Tsinghua University, Beijing 100084, China*
[7] *Department of Urban Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 1138656, Japan*
[8] *Department of Environmental Sciences, Faculty of Environmental Studies, Universiti Putra Malaysia, Serdang, 43400 UPM, Malaysia*
[9] *Research Center for Environmental Technology and Sustainable Development, Hanoi University of Science, 334 Nguyen Trai, Hanoi, Vietnam*

ABSTRACT

The most prevalent pollutant, polycyclic aromatic hydrocarbons (PAHs) is now plenteously distributed in the global atmosphere. We recently quantified 36 polycyclic aromatic hydrocarbons (PAHs) associated with aerosols (particulate matter: PM) in five Asian cities: Tokyo (Japan), Beijing (China), Kolkata (India), Hanoi (Vietnam), and Kuala Lumpur (Malaysia). Average atmospheric PAH concentrations ($\sum$12 PAHs-ng m^{-3}) increased in the order of Kuala Lumpur (2.99) ≈ Tokyo (3.95) < Hanoi (7.99) << Kolkata (63.5) << Beijing (142.8). The most abundant PAHs in PM samples in these cities were chrysene, benz[*a*]anthracene, benzofluoranthenes, benzo[*a*]pyrene, and benzo[*e*]pyrene. We used the PAH compositions, especially the relative abundances of alkylated PAHs, and hopanes to determine vehicle exhaust-derived PAHs, and levoglucosan as a tracer for biomass burning, especially from wood combustion. Vehicle exhaust contributed to atmospheric PAHs in all cities, indicated by higher ratios of ($C_{30}17\alpha$)/total PAHs and MPAHs/PAHs than coal and wood combustion products. Coal combustion contributed also in winter aerosols in Beijing, indicated by higher abundance of β isomers i.e., 17β21β (H)-C_{30}hopane ($C_{30}17\beta$) and 17β21β (H)-C_{29}hopane ($C_{29}17\beta$) signifying mass use of coal for heating. The ratio of levoglucosan/PAHs was high in Kuala Lumpur and Hanoi, suggesting greater inputs of PAHs from biomass burning there.

Keywords: Aerosol; PM; Coal combustion; Biomarkers; Hopanes; Levoglucosan.

INTRODUCTION

Rapid population growth and industrialization are placing pressure on the environment. One obvious effect is the proliferation of hazardous materials, such as polycyclic aromatic hydrocarbons (PAHs), in the atmosphere. PAHs cause great concern because of their mutagenic, carcinogenic, and teratogenic properties, and are designated as priority pollutants in the EU (IARC, 1983; Boeuf *et al*.., 2016). They tend to be associated with particulate matter (PM), soils, and sediments (EEA, 2012; Cassee *et al*., 2013; Cheruiyot *et al*., 2015). The mass of PM is a widely accepted parameter in air quality protocols (Cassee *et al*., 2013). Suspended PM can be evaluated by its size. PM_{10} (particles with aerodynamic diameter < 10 µm) has been associated with adverse health effects, although in recent times smaller cutoffs ($PM_{2.5}$ or PM_{10}) have been proposed as better indexes of air pollution

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[*] Corresponding author.
E-mail address: shige@cc.tuat.ac.jp

owing to greater lung deposition of smaller particles in association with toxic compounds (Varghese and Gangemma, 2006; Wiriya *et al.*, 2016). Since PAHs have affinity to the PM carbonaceous core, they are found mostly on smaller particles (Miguel *et al.*, 1998; de Kok *et al.*, 2005; Zhou *et al.*, 2005).

PAHs in urban air are dominated by various anthropogenic sources, with limited contribution from natural sources (forest fires, volcanic emissions etc.). PAHs are products of incomplete combustion and pyrolysis of fossil fuels (e.g., petroleum, gas, coal) and other organic materials (e.g., biomass). Hence, it is important to understand the abundance, speciation, distribution, and potential sources of PAHs in aerosols so that the diverse effects of PM can be efficiently controlled. The adverse properties of PAHs, together with their still growing emission to the environment, make their monitoring a top priority in the evaluation of both human health risk and environmental hazards (Chetwittayachan *et al.*, 2002; Saha *et al.*, 2012).

Emissions of PAHs to atmosphere in developing countries continue to increase owing to increases in population, industrial emissions, and vehicle emissions, along with poor urban management. A number of studies have focused on atmospheric PAHs in developing nations such as China, India, Hong Kong, and Thailand (Chetwittayachan *et al.*, 2002; Sun *et al.*, 2004; Ravindra *et al.*, 2006; Haggler *et al.*, 2007; Liu *et al.*, 2007; Okuda *et al.*, 2010; Masih *et al.*, 2012; Li *et al.*, 2016; Pongpiachan, 2016; Wiriya *et al.*, 2016; Yu *et al.*, 2016; Tang *et al.*, 2017; Zhou *et al.*, 2017). Some studies have reported that vehicular emissions are the primary cause of PAH pollution in many Japanese cities (Chetwittayachan *et al.*, 2002; Hayakawa, 2009; Murakami *et al.*, 2012). Beijing has instituted extensive work to monitor the quality of ambient air (Zhou *et al.*, 2008; Zhao *et al.*, 2011; Li *et al.*, 2013; Sun *et al.*, 2013; Bandowe *et al.*, 2014; Li *et al.*, 2016; Tang *et al.*, 2017). In 2011, the city burned 26.3 million tons of coal, 73% of which was used for heating and power generation, and the remainder for industry (China Daily, 2012). Consequently, the coal combustion had highest contribution to organic carbon (12.4 ± 4.6% of $PM_{2.5}$ mass) in Beijing-Tianjin-Hebei regions of China during wintertime (Zhou *et al.*, 2017). Emissions from coal-fired power plants and heating amenities are the major source of $PM_{2.5}$ PAHs. Atmospheric PAH levels in the Indian cities of Kolkata, Mumbai, and Chennai are higher than in other cities around the world (Cheng *et al.*, 2013), but are derived mainly from traditional biomass resources (Masih *et al.*, 2012). In other cities such as Hanoi, Vietnam, multitudes of large commercial vehicles and motorbikes contribute greatly to PAHs (Kishida *et al.*, 2008; Thuy *et al.*, 2012). The main source of PAHs in Kuala Lumpur, Malaysia, is vehicular emissions, since motor vehicles contribute as much as 82% of atmospheric pollutants (MEQR, 1996; 2007). During haze and clear episodes in Kuala Lumpur, high concentrations of PM_{10} PAHs are recorded, including benzo[*b*]fluoranthene and benzo[*k*]fluoranthene, which can be directly connected to biomass burning (Omar *et al.*, 2006). However, although there have been studies of atmospheric PAHs in individual Asian countries, there have been no comparative studies targeting multiple Asian countries under the same protocol. In particular, there has been no attempt to identify the primary sources or to quantify the atmospheric PAHs in multiple developing Asian countries on a seasonal basis.

In this study, we investigated the air particulate phase, especially PAHs, in Tokyo, Beijing, Kolkata, Hanoi, and Kuala Lumpur, which were chosen for their high anthropogenic impacts. Aerosol samples were collected seasonally during 2008–2011. Prior to the full-scale sampling in 2008–2011, the preliminary sampling was conducted in Asian countries in 1999–2004, to examine the phase distribution of PAHs.

Atmospheric PAHs can be formed by coal or wood combustion or by petroleum combustion. Petroleum-derived sources are evaluated by using hopane biomarkers (Zakaria *et al.*, 2000, 2001, 2002; Boonyatumanond *et al.*, 2006; Saha *et al.*, 2009, 2012; Yu *et al.*, 2016). Hopanes are pentacyclic C_{27} to C_{35} triterpenes and are ubiquitously present in crude oil. Owing to their high boiling point, hopanes are not found in fuel, but are found in lubrication oils, asphalt, and heavy residual oil. Hopanes with the 17α (H), 21β (H)-configuration are characteristic of petroleum as they are abundant and are thermodynamically stable compared with other epimeric (ββ and βα) series (Wang *et al.*, 2007).

Biomass combustion is a primary source of atmospheric organic PM and some trace chemical contaminants (Simoneit *et al.*, 1999). Usually, impacts from biomass burning is traced through the use of levoglucosan, resin acids, syringols, and retene (Simoneit *et al.*, 1999; Yan *et al.*, 2008). Levoglucosan (1,6-anhydro-β-D-glucopyranose), a major organic component emitted in fine smoke PM during pyrolysis of cellulose, can be used as a marker of biomass burning in samples of atmospheric PM (Simoneit *et al.*, 1999). Its use as a tracer indicated that biomass burning was the main source of organic aerosol PM during haze episodes in Malaysia (Abas *et al.*, 2004). Here, we used levoglucosan to distinguish sources of biomass burning in aerosol samples collected in the five cities.

The main objectives of this study were (1) to determine the level of PAH contamination in PM from the five cities; (2) to determine seasonal variations in PAH concentrations in each city; and (3) to identify the sources of atmospheric PAHs (petroleum derived or combustion derived) from the relative abundance of alkylated PAHs, hopane, and levoglucosan.

MATERIALS AND METHODS

Sampling Locations

Atmospheric aerosols were sampled in Tokyo (2010), Beijing (2008–09), Kolkata (2009–11), Hanoi (2009–10), and Kuala Lumpur (2010–11) (Fig. 1). The sampling sites were sited away from major roads and point-sources (e.g., waste disposal facilities, power plants) to avoid their direct influence on the representativeness of the samples. Information on the sampling sites is summarized in Table 1. Further details and the background information of study areas are described below.

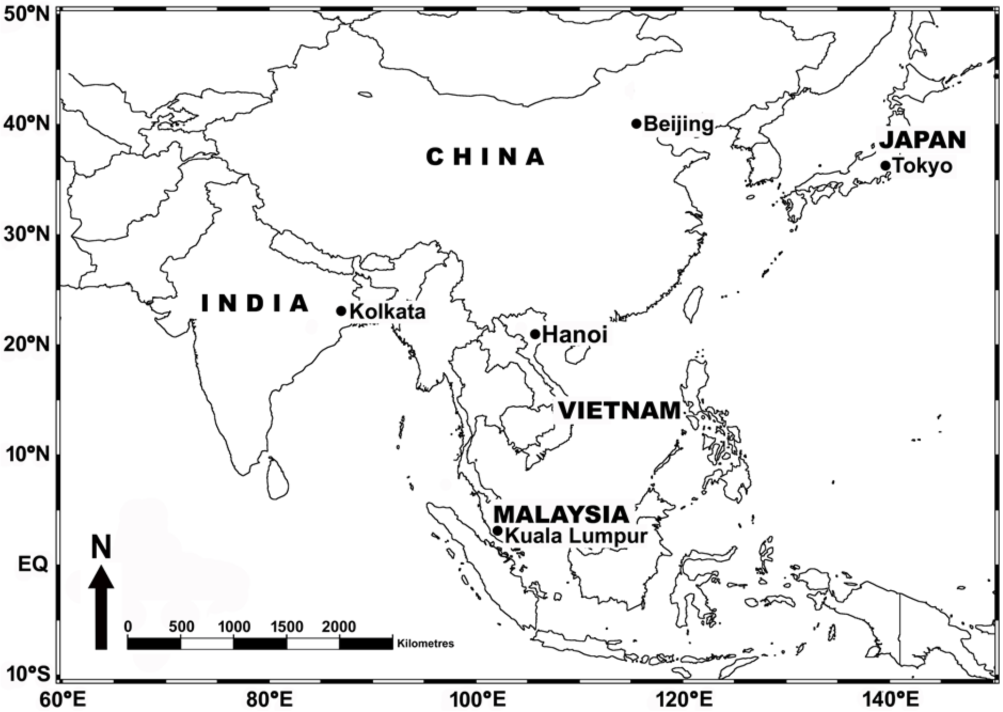

Fig. 1. Schematic map showing the geographical location of the sampling areas i.e., Tokyo, Beijing, Kolkata, Hanoi and Kuala Lumpur.

Tokyo is the capital and the most populous city of Japan, with a population of 13 million (2014). Samples were collected weekly from 5 January to 27 December 2010 on the roof (10th floor) of the 14th building on the Hongo campus of Tokyo University, on the outskirts of Tokyo, about 800 m from the nearest highway. Beijing is the capital and the second largest city in China, with a population of 21 million (2014). Samples were collected weekly from 2 October 2008 to 17 September 2009 at Tsinghua University, around 15 km from the city and 1 km from the nearest highway. Kolkata is the main commercial and financial center of eastern India, with a population of 15.55 million (2016). Samples were collected weekly during 2009–11 from two locations. In 2009–10, samples were collected from a residential area, 10 to 20 m from a main road. From 13 January to 23 December 2011, samples were collected from the roof of a four-story building in the Jadavpur University campus, 20 km from the center of Kolkata. Hanoi is the capital of Vietnam, in the north, with an estimated population of 7.7 million (2015). Samples were collected weekly from 6 October 2009 to 27 September 2010 on the balcony of a four-story house in a residential area about 4 km southwest of the city center, approximately 1 km from the nearest highway. Kuala Lumpur is the capital and most populous city of Malaysia, with an estimated population of 1.7 million (2015). Samples were collected monthly from September 2010 to December 2011 on a roof of University Putra, 15 km from the city and 1 km from the main street.

Prior to the full-scale sampling in 2008–2011, the preliminary sampling was conducted in Asian countries including Japan, India, Malaysia, and Vietnam in 1999–2004, to examine the phase distribution of PAHs. The samples are listed in Table S1 (Supporting Information). Original data in Japan (Tokyo) collected in 2001 are from our previous publication (Murakami *et al*., 2012).

Sampling Procedures

The Aerosol samples were collected with high-volume (HV) air samplers: Kimoto Model 120 in Beijing, and SibataHV-1000F in Tokyo, Kolkata, Hanoi, and Kuala Lumpur. During the preliminary sampling in 1999–2004, TFIA-2 high-volume air sample (Staplex, USA) was employed. PM was trapped on pre-baked quartz filters (Pallflex membrane filter 2500QAT-UP, 200 mm × 250 mm). Air was filtered continuously at 800–1000 L $\min^{-1}$, and filters were collected weekly for a year, except in Kuala Lumpur, where PM was collected for 24 h once a month. The collected filters were wrapped in aluminum foil and stored in press-seal bags at –30°C. During the preliminary survey, through the phase-partitioning study in 1999-2004, three pieces of polyurethane foam (PUF; Shibata 8013-0941A polyurethane for dioxin, 5 cm × 6 cm i.d.) was plugged in series after the quartz filter to collect the gaseous PAHs. The collected PUF was wrapped in aluminum foil and stored in press-seal bags at –30°C. When an additional piece of PUF was installed to examine the trapping efficiency of PAHs, no significant amounts of PAHs (< 1% of total PAHs trapped by 4 pieces of PUFs) were detected in the fourth PUF (Table S2), hence, the three PUF was analyzed to measure gas-phase PAHs in the phase-partitioning study.

Analytical Process

Weekly filter samples (but not monthly Kuala Lumpur samples) were bulked as monthly composite samples for

Table 1. Sampling Information on Air samples on the full-scale survey in Asia.

Sample code	Country	City (district)	Specific location	Location type	Sampling duration	Cordinate	Remark
Tokyo	Japan	Tokyo	14th building of University of Tokyo	Downtown	Jan. 2010–Dec. 2010	N 35.714024 E 139.759512	28 m from the ground
Beijing	China	Beijing	Tsinghua University	Downtown	Oct. 2008–Sept., 2009	N 40.005991 E 116.319613	5 m from the ground
Kolkata-1	India	Kolkata	Beleghata, Residetial place	Downtown	Dec, 2009–Nov 2010	N 22.562752 E 88.397603	2nd floor balcony of two-story-building
Kolkata-2	India	Kolkata	Jadapur University	Downtown	Jan, 2011–Dec 2011	N 22.496242 E 88.371681	Roof of a four-story building
Hanoi	Vietnam	Hanoi	Trung Yên 9, Quan Cau Giay, Cầu Giấy	Downtown	Oct, 2009–Sept 2010	N 21.01600 E 105.80205	4th floor balcony of four-story-building
Kuala Lumpur	Malaysia	Kuala Lumpur	Faculty of Environmental Studies Building, University Putra Malaysia	Suburb	Sept. 2010–Dec 2011	N 3.004611 E 101.709111	Roof of the three-story building

extraction. The filters were extracted with DCM/MeOH (95:5 *v/v*) in an accelerated solvent extractor (ASE300; Dionex, Japan) in 3 cycles of pre-heat for 0 min, hold for 5 min, flush 50%, purge for 1 min, at a constant 6.9 MPa and 100°C. The extract was concentrated in a rotary evaporator and spiked with 50–100 μL of 5 ng μL^{-1} of deuterated PAHs (naphthalene-d_8, anthracene-d_{10},*p*-terphenyl-d_{12}, benzo[*a*]anthracene-d_{12}, and perylene-d_{12}) as surrogates, and then purified by silica gel chromatography. No surrogates were added for the hopane fraction. Details of the chromatography are described in Boonyatumanond (2006). Silicagel (5% water deactivated) column chromatography was used to eliminate polar components. Alkanes + hopanes and PAHs were fractionated through a fully activated silica gel column. The PAH fraction was analyzed by gas chromatograph (GC-MS, 6890N; Agilent Technologies, Santa Clara CA, USA) coupled to a mass selective detector (5973; Agilent Technologies) programmed as follows: initial temperature 70°C for 2 min, ramp to 150°C at 30 °C min^{-1} then to 310°Cat 4 °C min^{-1}, and hold for 10 min.

Identification and quantification were performed in selected ion monitoring (SIM) modeas described in Saha *et al.* (2009). The following 36 compounds were analyzed: phenanthrene(Phe), anthracene (Anth), 4H-cyclopenta[*def*]phenanthrene (CPP), 3-methylphenanthrene (3-MP), 2-MP,9-MP, 1-MP, fluoranthene (Fluo), pyrene (Py), 3,5-dimethylphenanthrene (3,5-DMP), 2,6-DMP, 1,7-DMP, 1,6-DMP, methylpyrenes or methylfluoranthenes (MPy with prefix of a- to d-, in order of elution), benzo[*a*]anthracene (BaA), chrysene (Chry), retene(ret), methylchrysene or methylbenz[*a*]anthracene (MC with prefix of e- to i-, in order of elution), benzo[*b*]fluoranthene (BbF), BjF+BkF, BeP, BaP, perylene(Pery), indeno[1,2,3-*cd*]pyrene (IndPy), benzo[*ghi*]perylene (BghiP), dibenzoanthracene (DBA), coronene (Cor), and 1,3,5-triphenyl benzene(TPB). The sum of all 36 species is expressed as ∑36 PAHs. To make a comparison of our values with literature data, sum of major 12 parent PAHs, i.e., Phe, Anth, Fluo, Py, BaA, Chry, BbF, BkF(BjF), BaP, IndPy, BghiP, DBA was calculated as ∑12 PAHs (Table 2). Concentrations were recovery-corrected with spiked surrogates (consistently > 80%). Reproducibility in four replicate analyses was 1% to 19% relative standard deviation. Procedural blanks were run in each batch, and analytical values ≥ 5× the blank were considered as significant. For the phase-distribution study, PUFs were extracted with DCM by Soxhlet extraction for ~12 h and analyzed similarly as filter samples.

To the hopane fraction, we added 50 to 200 μL of 2 ng μL^{-1} of 17β(H), 21β(H) hopane in *iso*-octane as an internal injection standard, and analyzed the extracts by GC-MS (5973A) programmed to hold at 70°C for 2 min, ramp to 150°C at 30 °C min^{-1} then to 310°C at 5 °C min^{-1}, and hold for 6 min, in SIM mode at *m/z* = 191. The following 18 hopane homologs and isomers were measured: 18α(H),21β(H),22,29,30-trisnorneohopane [Ts]; 17α(H),21β(H), 22,29,30-trisnorhopane [Tm]; 17α(H),21β(H)-norhopane [C_{29}17α]; 18α(H)-30-norneohopane [C_{29}18α]; 17β(H),21α(H)-norhopane [C_{29} 17β]; oleanane; 17α(H),21β(H)-hopane [C_{30}17α];

Table 2. Atmospheric PAHs, hopane and levoglucosan of five Asian mega cities with average and minimum to maximum range of data.

Parameters	Tokyo	Beijing	Kolkata	Hanoi	Kuala Lumpur
∑36 PAHs (ng m^{-3})	5.28 (2.37–9.34)	229.96 (22.76–774.08)	92.83 (17.54–327.4)	11.64 (4.06–28.77)	5.74 (3.44–10.35)
∑12 PAHs (ng m^{-3})	3.95 (1.64–6.79)	142.79 (15.38–496.72)	63.49 (12.56–228.86)	7.99 (2.56–21.49)	2.99 (1.88–4.76)
HMW-PAHs	2.76 (1.44–5.04)	78.4 (13.05–236.01)	64.33 (12.91–219.71)	8.21 (3.3–16.06)	4.8 (2.82–9.15)
B[a]P	0.38 (0.17–0.57)	13.47 (0.86–51.3)	6.48 (1.14–22.35)	0.57 (0.18–1.81)	0.23 (0.09–0.43)
MP/P	0.49 (0.44–0.63)	0.78 (0.58–1)	0.47 (0.35–0.52)	0.54 (0.38–0.67)	0.65 (0.56–0.81)
MPy/Py	0.11 (0.09–0.14)	0.25 (0.11–0.64)	0.15 (0.09–0.24)	0.16 (0.11–0.24)	0.17 (0.14–0.23)
MC/C	0.28 (0.21–0.36)	0.5 (0.32–0.8)	0.40 (0.32–0.52)	0.38 (0.27–0.51)	0.7 (0.53–0.86)
MPAHs/PAHs	0.23 (0.21–0.28)	0.4 (0.3–0.53)	0.32 (0.23–0.4)	0.31 (0.22–0.42)	0.51 (0.39–0.67)
Pyr/Fluo	0.8 (0.72–0.9)	0.85 (0.78–1.04)	1.06 (0.97–1.17)	0.98 (0.83–1.15)	0.16 (1.08–1.28)
Anth/(Anth + Phe)	0.13 (0.05–0.47)	0.07 (0.04–0.1)	0.12 (0.09–0.15)	0.09 (0.05–0.14)	0.15 (0.13–0.17)
BaA/(BaA + Chry)	0.3 (0.24–0.38)	0.31 (0.22–0.45)	0.32 (0.28–0.36)	0.27 (0.25–0.32)	0.32 (0.22–0.38)
IP/(IP + BghiP)	0.44 (0.42–0.47)	0.44 (0.36–0.47)	0.44 (0.41–0.46)	0.42 (0.39–0.46)	0.39 (0.34–0.41)
∑Hopane (ng m^{-3})	1.99 (1.18–3.55)	20.16 (3.83–53.29)	43.14 (10.24–86.95)	2.11 (1.37–2.8)	5.33 (3.94–6.52)
Hopane/PAHs	0.43 (0.27–0.92)	0.21 (0.07–0.42)	0.78 (0.35–1.76)	2.26 (0.1–0.46)	1.37 (0.89–2.13)
∑Levoglucosan (ng m^{-3})	36.17 (3.5–91.64)	269.5 (21.9–816.7)	1053.03 (18.3–2367.8)	471.81 (143.1–1051)	162.69 (89–330)
Levoglucosan/PAHs	5.7 (0.8–11.74)	1.25 (0.23–2.14)	11.51 (2.38–18.89)	30.98 (11.8–53.3)	28.12 (17–41.9)
$\sum C_{30}$ 17α/C_{30} 17β	8.01 (6.61–9.45)	2.96 (0.92–4.65)	4.12 (2.29–6.5)	5.84 (4.92–6.8)	7.49 (4.53–10.39)

17β(H),21α(H)-hopane [C_{30}17β]; and C_{31} to C_{35} homohopanes with S and R stereo-isomers at C-22 [C_{31} to C_{35}]. Individual hopanes were identified by comparison of the retention times with those of internal injection standards (IISTDs) and authentic standards (Tm, C_{29}17α, C_{29}17β, C_{30}17α, C_{30}17β, 18α(H)-oleanane, C_{31}17α). They were quantified by comparing the integrated peak area of the selected ion at *m/z* = 191 with that of the IISTD.

To analyze levoglucosan, we extracted the samples with ethyl acetate in the ASE300, in 3 cycles of pre-heat for 5 min, static 5min, flush 90%, purge 1.3 min, at 10.3 MPa and 100°C. The extract was concentrated, spiked with surrogate (sedoheptulosan in MeOH), and dried in a stream of N_2. The extract was re-dissolved in 50 µL of pyridine, followed by the addition of *N,O*-bis-(trimethylsilyl)trifluoroacetamide containing TMS, and was derivatized by heating at 70°C for 2 min a sealed aluminum block. After cooling, acenaphthene-d_8 and chrysene-d_{12}in *iso*-octane solution were added as IISTD, followed by GC-MS as follows: 2 min hold at 70°C, ramp to 150°C at 30 °C min^{-1}, then to 270°C at 4 °C min^{-1}, then to 310°C at 30 °C min^{-1}, and hold for 7 min. The following ions were monitored in SIM mode: *m/z* = 128, 136 (acenaphthene-d_8), *m/z* = 73, 204, 217, 333 (levoglucosan), *m/z* = 73, 204, 217, 239 (sedoheptulosan), and *m/z* = 240 (chrysene-d_{12}). Peaks were identified by comparison of the retention time with the IISTD. Components were quantified as the ratio to the peak area of the IISTD and the extracted target compound ions of *m/z* = 162, 204, 240. Recoveries were 98% ± 4% of the surrogate and 105% ± 3% of levoglucosan. Reproducibility was 2%.

RESULTS AND DISCUSSION

Phase Distribution of PAH Species between Gas and Particulate Phases

Table S3 depicts the distribution of PAHs between gas and particulate phases in Asian countries including Japan, India, Malaysia, Vietnam, and Cambodia. As indicated by previous researchers (Yamasaki *et al.*, 1982; Lighty *et al.*, 2000; Cheruiyot *et al.*, 2015; Li *et al.*, 2016; Paolini *et al.*, 2016; Pongpiachan *et al*., 2016), lower molecular weight species partition more in gas phase, whereas higher molecular weight species distribute more in particulate phase, depending on their vapor pressure. For example, phenanthrene (three-ring species) was predominantly present in gas phase with percent particulate ranging from 1% to 15% (Table S3 and Fig. SI1), whereas benzo[b]fluoranthene (five-ring species) was present exclusively in the particulate phase, (with percent particulate > 90% except for two samples). Partitioning of 4-ring species such as pyrene and chrysene was intermediate and variable depending on ambient temperature. As illustrated in Fig. S1, they distributed less in particulate phase during warmer season with air temperature around 25°C than in winter season. In tropical Asian countries such as Malaysia, significant fraction, i.e., ~50%, of chrysene was present in gas phase (Table S3). This is due to higher ambient temperature in the tropical area. In addition, abundance of particles in the air controls the partitioning and more PAHs were present in particulate phase in the locations with higher total suspended particles. For example, in India, more than 80% of chrysene was present in particulate phase, though it is situated in tropical area with ambient temperature around 30°C. It was demonstrated in previous researches (Yamasaki *et al*., 1982; Cheruiyot *et al*., 2015; Zhang *et al*., 2015) that the partitioning can be modeled using ambient temperature, total suspended solid, and compound-specific partition coefficient. However, the present study did not aim to model the partitioning but to provide information on temporal and spatial variability of toxicologically-important species, i.e., carcinogenic PAHs, and to identify the sources of PAHs in Asian countries. Because toxicologically-important PAH species have 5 or more benzene rings such as BaP, the discussion in the later sections focus on higher molecular weight species. To facilitate our discussion, sum of higher molecular weight species ("HMW-PAHs"), i.e., BbF, BkF + BjF, BeP, BaP, IndPy, BghiP, coronene, DBA, and TPB were used. HMW-PAHs include carcinogenic species such as BbF, BaP, IndPy, and DBA. These higher molecular weight PAHs were distributed predominantly in particulate phase, regardless of areas and seasons. Thus, in the full-scale sampling, only particulate matter was analyzed.

Spatial Pattern of PAHs

∑36 PAHs were 2.4–9.3 ng m^{-3} in Tokyo, 23–774 ng m^{-3} in Beijing, 18–327 ng m^{-3} in Kolkata, 4.1–29 ng m^{-3} in Hanoi, and 3.4–10 ng m^{-3} in Kuala Lumpur (Table 2). ∑36 PAHs increased in the order of Tokyo < Kuala Lumpur < Hanoi << Kolkata << Beijing (Fig. 2). Similar spatial patterns were observed in terms of HMW-PAHs and ∑12 PAHs (Table 2). The average BaP concentration at Tokyo, Beijing, Kolkata, Hanoi and Kuala Lumpur was 0.38, 13.47, 6.48, 0.57 and 0.23 ng m^{-3} respectively (Table 2). BaP has been widely used as an indicator of total PAHs in the inhalation risk assessment due to its high carcinogenicity and atmospheric presence. The BaP value for Beijing and Kolkata were mostly exceeding 1.0 ng m^{-3}, the limit of the annual average BaP in the NAAQS (GB 3095-2012).

Throughout the year, ∑36 PAHs was high in Beijing, even at its lowest in June (23 ng m^{-3}). The highest concentration of PAHs in Beijing is comparable to previous study (e.g., 116 ng m^{-3}; Zhou *et al*., 2005). Although many of the previous studies also found higher PAHs in Beijing than in other cities of China (Liu *et al*., 2014; Liu *et al*., 2015; Yu *et al*., 2016), in a recent study, source control measures implemented by the city to diminish concentrations of atmospheric PAHs in Beijing (Tang *et al*., 2017).

In Kolkata, PAHs concentrations were highest in winter (Fig. 3), as reported previously (Cheng *et al*., 2013). Samples collected during 2010 in a residential area near a moderately trafficked main road (Kolkata 1) had more vehicle-derived PAHs than samples collected in 2011 from Jadavpur University, around 500 m from a highly trafficked main road (Kolkata 2) (Fig. 3). Values were high in Kolkata 1 samples, with large monthly variations (nearly 4×). Since vehicles exert a strong influence, we used samples from Kolkata 2 to better represent Kolkata.

Tokyo had the lowest ∑36 PAHs (Fig. 2), despite its huge energy consumption and large numbers of vehicles, on account of regulations such as the Clean Air Act. To avoid the direct contribution of nearby local sources, we collected samples at 28 m above the ground. To confirm that the sampling height did not affect the results, we collected samples from 28 m and 13 m at the same time. The concentration and composition did not differ between heights, so we considered the samples collected at 28 m to be representative of Tokyo.

∑36 PAHs in Hanoi (4.1–29 ng m^{-3}) was much lower than those in Beijing and Kolkata (Fig. 2). Kuala Lumpur had an average annual concentration of 5.74 ng m^{-3} (3.4–10 ng m^{-3}; Table 1; Fig. 2), close to the value of 5.85 ng m^{-3} recorded in Petaling Jaya, a major Malaysian city (Omar *et al*., 2006).

The PAHs in Beijing were dominated by Fluo, Py, BaA, Chry, Benzofluoranthenes, BeP, BaP, IndPy, and BghiP (Fig. SI2) is comparable to previous results (Zhou *et al*., 2009). The PAHs in Kolkata, Hanoi and Kuala Lumpur were dominated by Benzofluoranthenes, BeP, IndPy, and BghiP. High values of coronene distinguished Kuala Lumpur and Hanoi from Kolkata.

Seasonal Variations in PAH Concentrations

PAH concentrations varied substantially over seasons in all five cities (Fig. 3). Concentrations increased during winter (October–February) in Beijing, Kolkata, Hanoi, and Tokyo but increased during the warmer seasons (March–October) in Kuala Lumpur (Fig. 3). Similar trends have been reported in other studies (Varder *et al*., 2008; Morville *et al*., 2011; Yu *et al*., 2016) The ratios of ∑36 PAHs in winter (October–February) to those in the rest of the year were 16 in Beijing, 7.8 in Kolkata, 2.6 in Hanoi, 1.4 in Tokyo, and 0.8 in Kuala Lumpur.

Relatively higher temperature, humidity and wind speed in summer also led to stronger photolysis and dispersion of PAHs (Yang *et al*., 2010). Generally, in the warmer seasons, more PAHs are partitioned from PM into the gaseous phase owing to the higher temperatures, decreasing the concentrations in PM. To cancel the seasonal change in phase distribution, seasonal trends of HMW-PAHs, which

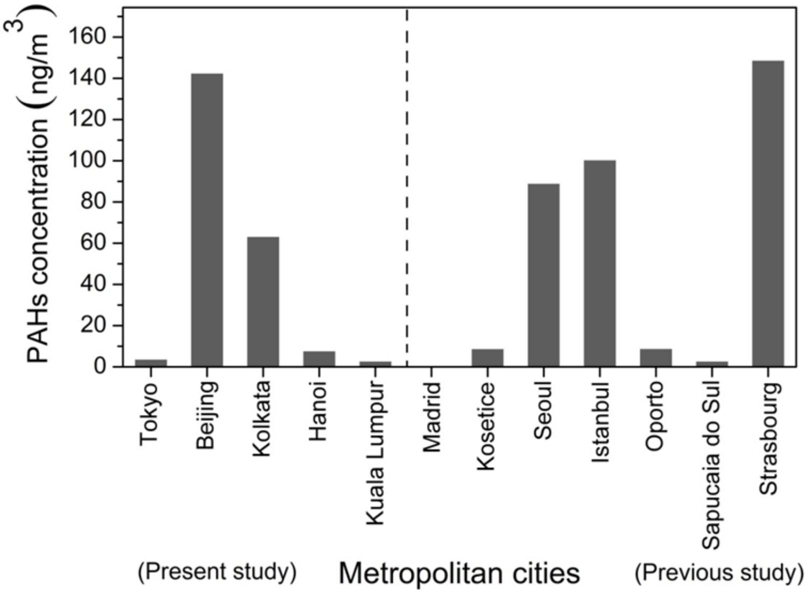

Fig. 2. Total PAHs in aerosols of metropolitan cities around the world: a comparison of present study (∑12 PAHs) (Tokyo, Beijing, Kolkata, Hanoi and Kuala Lumpur) with previous studies (∑14 PAHs- ∑17 PAHs) i.e., Madrid (Barrado *et al.*, 2012), Kosetice (EMEP, 2010; Dvorská *et al.*, 2012) Seoul (Park *et al.*, 2002), Istanbul (Hanedar *et al.*, 2014), Oporto (Slezakova *et al.*, 2013), Sapucaia do Sul (Agudelo-Castañeda *et al.*, 2014), Strasbourg (Morville *et al.*, 2011).

are exclusively distributed in PM regardless air temperature, are shown in Fig. 3. Similar seasonal trends were observed for HMW-PAHs, though the differences between the winter and the rest of the seasons were smaller for HMW-PAHs than ∑36 PAHs. For example, the winter-rest ratio for HMW-PAHs was 6.8 and 6.3 in Beijing and Kolkata, respectively, while it was 16 and 7.7 for ∑36 PAHs. These indicate that there must be some other mechanisms for the seasonal trends. Warm-season rains can washout PM from the atmosphere, producing lower concentrations of PAHs (Sharma *et al.*, 2007). Beijing experiences high rainfall in June–August, when the average ∑36 PAHs was 26.1 ng m^{-3}, which was much lower than in winter (Fig. 3). Similarly, the southwest monsoon, stretches from July to the end of September brings heavy rain to Kolkata, lowering the average concentration to 10.5 ng m^{-3} (Fig. 3). Heavy rains in Hanoi from June to September reduced the average concentration to 6.27 ng m^{-3}, comparable to the average value in Tokyo (5.8 ng m^{-3}) during the rainy season. In Kuala Lumpur, rain was plentiful from November to March, and reduced the average concentration to only 4.96 ng m^{-3}. Both direct and indirect photo-degradation of PAHs in the atmosphere is more active during the warmer seasons (Sharma *et al.*, 2007; Tham *et al.*, 2008), explaining some of the lower PAH concentrations then. Furthermore, atmospheric inversions in winter raise PAH concentrations. In temperate Tokyo and Beijing, increased consumption of fuel for heating during winter contributes extra PAHs. This may also apply in Hanoi, but not in tropical Kolkata or Kuala Lumpur.

Sources of PAHs

We evaluated the ratios of methylated PAHs to parent PAHs to estimate the relative contributions of petroleum combustion and coal and wood combustion. These ratios were separately calculated as the ratios of methylphenanthrenes to phenanthrene (MP/P), methyl pyrene to pyrene (MPy/Py), methyl chrysene to chrysene (MC/C), and methyl PAHs to parent PAHs (MPAHs/PAHs) (Table 1; Fig. 4). Parent PAHs are thermodynamically more stable than alkylated PAHs (Blumer, 1976). During combustion at high temperatures such as coal and wood combustions, alkyl PAHs is exhausted. Butin petroleum, which is diagenetically generated at low temperatures in the crust, they remain in abundance (Saha *et al.*, 2009, 2012). Thus, mixing of residual petroleum components with combustion products created higher ratios of methyl PAHs to parent PAHs in vehicle exhaust, whereas coal and wood combustion produced lower ratios (Fig. 4). These ratios are described in our previous studies (Saha *et al.*, 2009, 2012), which show that vehicle exhausts have high values of these ratios (MP/P > 3.5, MPy/Py > 1.5, MC/C > 2.0, MPAHs/PAHs > 2.2), whereas high-temperature combustion of coal and wood produces low ratios (MP/P < 0.5, MPy/Py < 0.15, MC/C < 0.2, MPAHs/PAHs < 0.3).

Beijing (non-winter samples), Kolkata, Hanoi, and Kuala Lumpur had significant PAH contributions from vehicle exhaust, because MPAH/PAH was higher than the threshold of high-temperature combustion of coal and wood (0.3) (Fig. 4). Contributions were highest in Beijing (non-winter samples) and Kuala Lumpur. Kolkata had more PAHs derived from coal and wood combustion than from vehicle exhaust, whereas Beijing and Kuala Lumpur had the converse. However, PAHs in Tokyo originated mainly from high-temperature combustion. To investigate further, we also evaluated the specific sources of individual PAH homologs by based on MP/P, MC/C, and MPy/Py. MP/P ratios were 0.4–0.6 in Tokyo, 0.6–1 in Beijing, 0.4–0.5 in Kolkata, 0.4–0.7 in Hanoi, and 0.6–0.8 in Kuala Lumpur

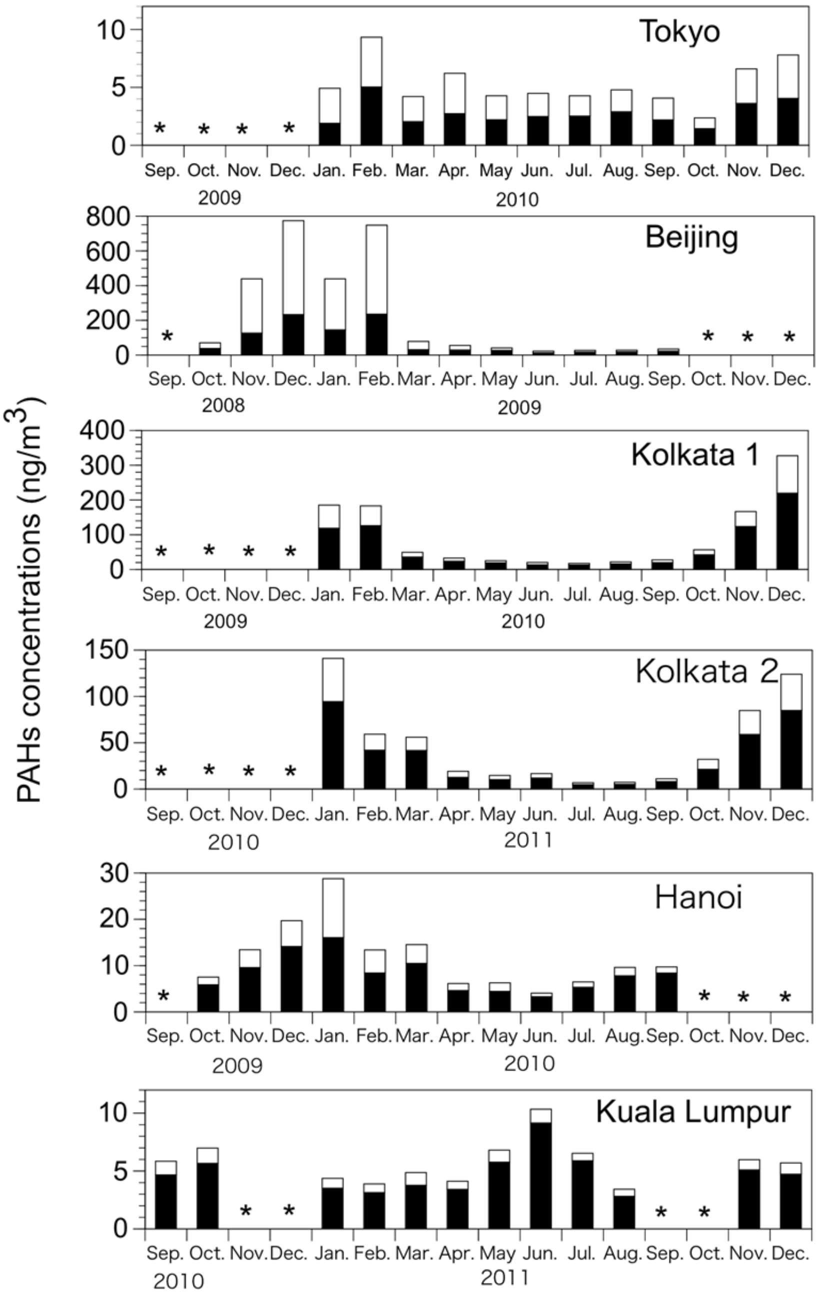

Fig. 3. Seasonal variation of PAHs in aerosols from the five Asian metropolitan cities. Solid bar: HMW-PAHs (sum of BbF, BkF + BjF, BeP, BaP, IndPy, BghiP, coronene, DBA, and TPB); Cumulative bar (solid bar + open bar): ∑36 PAHs; * denotes unavailability of data.

(Table 1). MP/P ratios in all cities were higher than those of most coal and wood combustion products, so vehicle exhaust had a greater influence than high-temperature combustion, probably owing to the high abundance of lower-molecular-weight PAHs, including phenanthrene, in petroleum (Saha *et al.*, 2009).

MPy/Py ratios were 0.09–0.14 in Tokyo, 0.11–0.64 in Beijing, 0.09–0.24 in Kolkata, 0.11–0.24 in Hanoi, and 0.14–0.23 in Kuala Lumpur. MC/C ratios were 0.21–0.36 in Tokyo, 0.32–0.8 in Beijing, 0.32–0.52 in Kolkata, 0.27–0.51 in Hanoi, and 0.53–0.86 in Kuala Lumpur (Table 1; Fig. 4). Overall, all cities showed more input of Py and Fluo derived from coal or wood combustion than from vehicle exhaust, except Beijing in winter, with a significant contribution of vehicle-derived PAHs. Similarly, the MC/C ratios of all cities were greater than the threshold (MC/C > 0.2), possibly because of a significant contribution of vehicle exhaust along with combustion-derived sources of PAHs.

We also evaluated the Py/Fluo, Anth/(Anth + Phe), BaA/(BaA + Chry), and IP/(IP + BghiP) ratios to assess sources of PAHs. In all cities, Py/Fluo ≤ 1 and BaA/(BaA+ Chry) ≤ 0.35 (Table 1), signifying a greater contribution of combustion-derived PAHs (Yunker *et al.*, 2002). On the

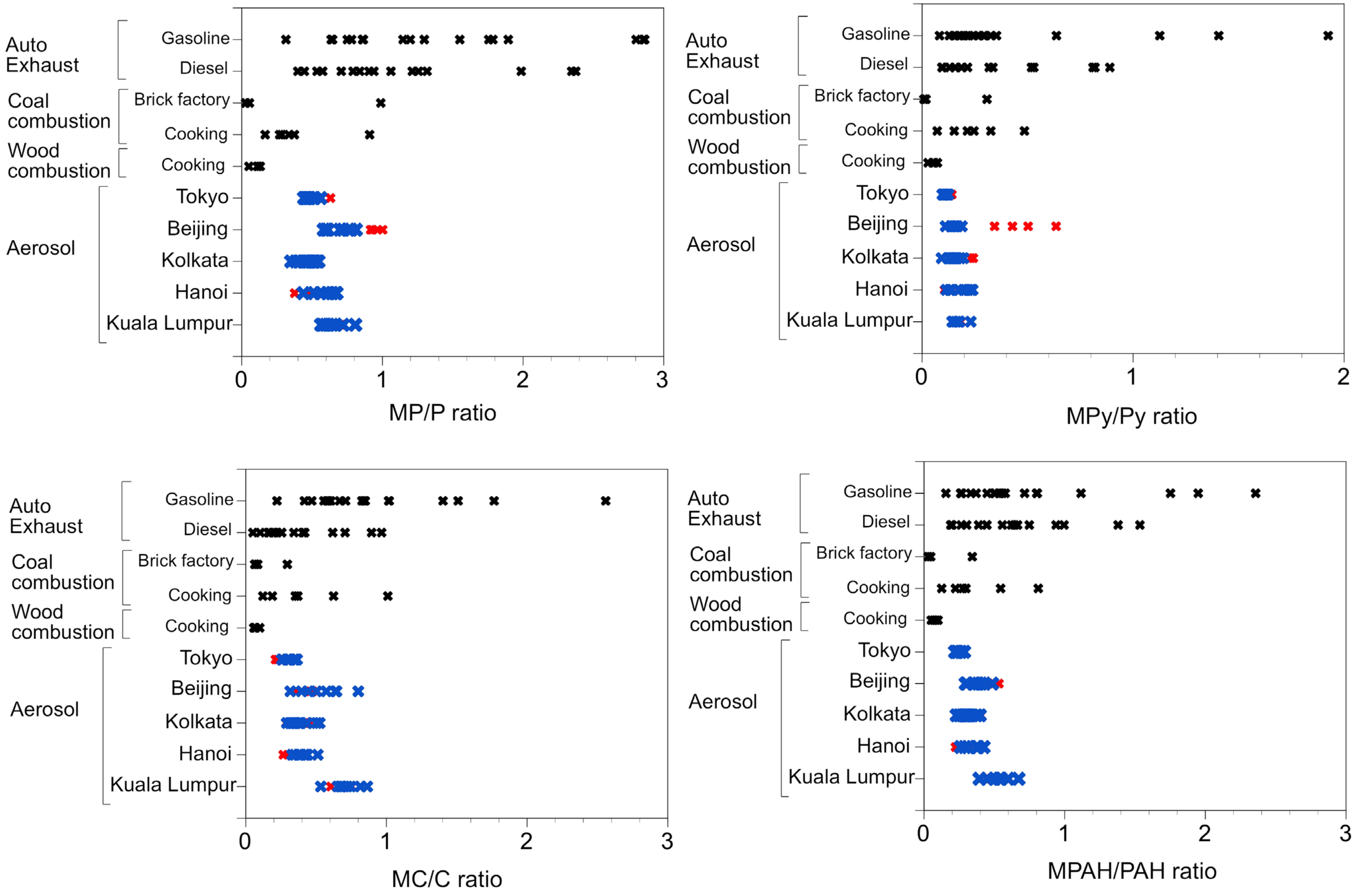

Fig. 4. Comparison of the ratios (a) MP/P, (b) MPy/Py, (c) MC/C and (d) MPAHs/PAHs in aerosol samples with that of source materials from the metropolitan cities of Asia. *(The blue and red points are indication the value of ration for aerosol in non-winter and winter season respectively).*

other hand, in most cases, Anth/(Anth + Phe) ≤ 0.1 and IP/(IP + BghiP) < 0.5, indicating that the contribution of vehicle exhaust in all cities cannot be ignored.

We could not clearly identify any particular sources from these compositional ratios. Hence, we used hopanes as petroleum markers and levoglucosan as a biomass marker to trace the sources of the atmospheric PAHs.

Hopanes

The total hopane concentrations were 1.2–3.6 ng m^{-3} in Tokyo, 3.8–53 ng m^{-3} in Beijing, 10–87 ng m^{-3} in Kolkata, 1.4–2.8 ng m^{-3} in Hanoi, and 3.9–6.5 ng m^{-3} in Kuala Lumpur (Table 1). We compared hopane profiles from three source materials (wood soot, coal soot, and vehicle soot) with those in the aerosol samples from the five cities (Fig. SI3). The relative compositions of hopanes did not differ greatly among the cities, and showed the predominance of 17α21β(H)-C_{30}(C_{30}17α) and 17α21β(H)-C_{29}(C_{29}17α) hopanes throughout the year, as in vehicle-related sources with the exception of Beijing in winter (Fig. SI3). The higher abundance of β isomers (17β21β(H)-C_{30}[C_{30}17β] and 17β21β(H)-C_{29}[C_{29}17β]hopanes) in winter aerosols of Beijing are identical to those in coal soot, in correspondence with the mass usage of coal during winter. Hopanes are generally found in petrogenic sources, but can be used as biomarkers of coal as well (Oros and Simoneit, 2000; Simoneit *et al.*, 2007; Saha *et al.*, 2012). The abundance of β homologues in the hopane profiles indicates a clear demarcation between coal-combustion-related hopanes and vehicle-exhaust-related hopanes; β isomers are usually found in higher abundance in coal-combustion-derived source than in vehicle-derived sources (Saha *et al.*, 2012). Hence, higher abundance of β isomers in winter in Beijing corresponds with the greater combustion of coal in Beijing during winter. In the other four cities, the hopane profiles were more similar to that of vehicle-related sources, suggesting less contribution from coal-combustion there.

Comparison of the (C_{30}17α/$C_{30}17_{β}$) ratios of each city with those of source materials (vehicle exhaust, > 4; coal/wood combustion, < 2.5; Saha *et al.*, 2012) revealed that all five cities had large contributions from petroleum-combustion (mainly vehicle exhaust) (Fig. 5). Other than winter samples from Beijing and a few non-winter samples from Kolkata, aerosols showed the predominant contribution of vehicle exhaust. Inputs from vehicle exhaust increased in the order of Beijing < Kolkata < Hanoi < Kuala Lumpur < Tokyo.

A very distinctive seasonal variation was found in Beijing, with a very low ratio of (C_{30}17α/C_{30}17β) during winter (November–February) followed by a rapid elevation (Fig. SI4). This low ratio is consistent with the relatively high PAHs concentrations during winter. The ratio remained very high during March–October in Beijing, signifying enhanced input of vehicle-related sources in non-winter season. In the other cities, however, no prominent seasonal variation in (C_{30}17α/C_{30}17β) was observed. Vehicle-related sources were dominant in Tokyo, Hanoi, and Kuala Lumpur, and co-dominant with coal-combustion-derived sources in Kolkata.

To understand and detect the contribution of vehicle exhaust or other petroleum-derived sources towards PAHs, we compared the ratio (C_{30}17α/total PAHs) from each city with those of various source materials from Saha *et al.* (2012). Kuala Lumpur had strong vehicle-related contributions, followed by Tokyo (Fig. 6). Diesel cars, gasoline cars, and motorbikes were the primary sources of petroleum-combustion-derived inputs in all five cities. High-temperature combustion of coal made substantial contributions in Beijing and Kolkata, but less in Hanoi. The very high consumption of coal in Beijing and Kolkata could explain the higher concentrations of PAHs in these two cities.

Levoglucosan

The concentrations of levoglucosan were 3.5–92 ng m^{-3} in Tokyo, 22–817 ng m^{-3} in Beijing, 18–2370 ng m^{-3} in Kolkata, 143–1050 ng m^{-3} in Hanoi, and 89–330 ng m^{-3} in Kuala Lumpur (Fig. 7(a)). Higher concentrations during

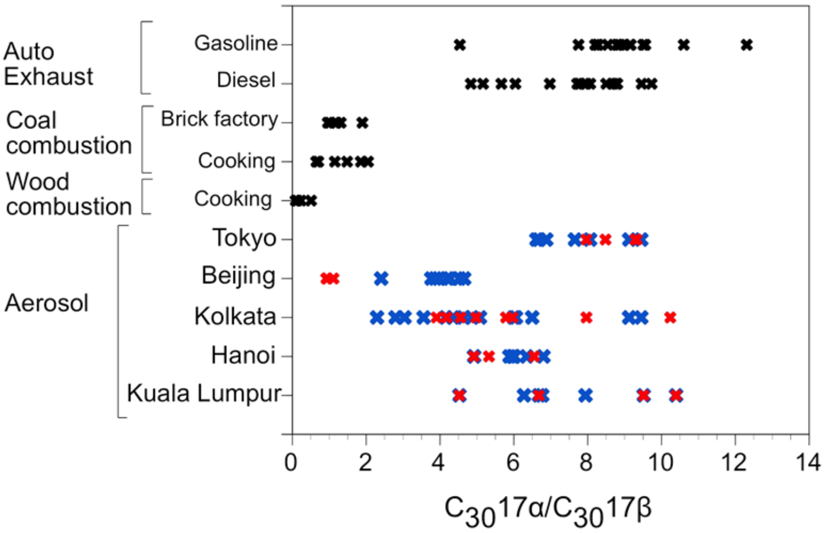

Fig. 5. Comparison of the ratio C_{30}17α/C_{30}17β in aerosol samples with that of source materials from the metropolitan cities of Asia. *(The blue and red points are indicating the value of ratios for aerosol in non-winter and winter season respectively).*

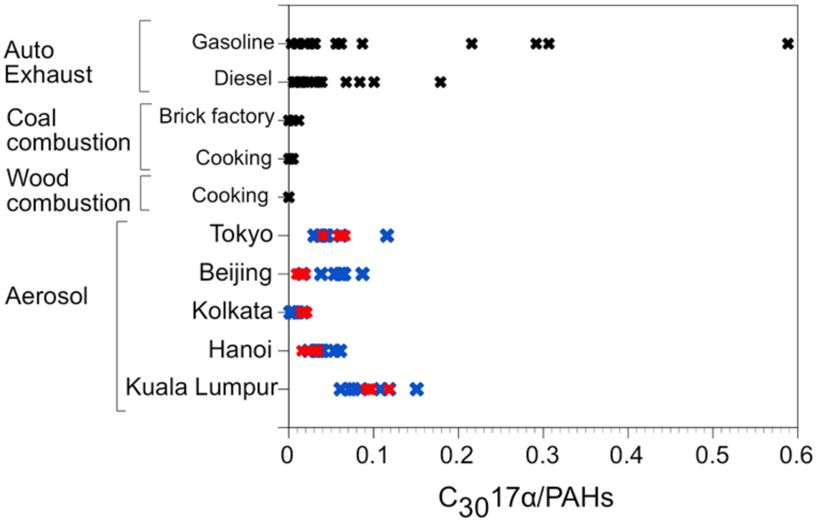

Fig. 6. Comparison of the ratio C_{30}17α Hop/PAHs in aerosol samples with that of source materials from the metropolitan cities of Asia. *(The blue and red points are indicating the value of ratios for aerosol in non-winter and winter season respectively).*

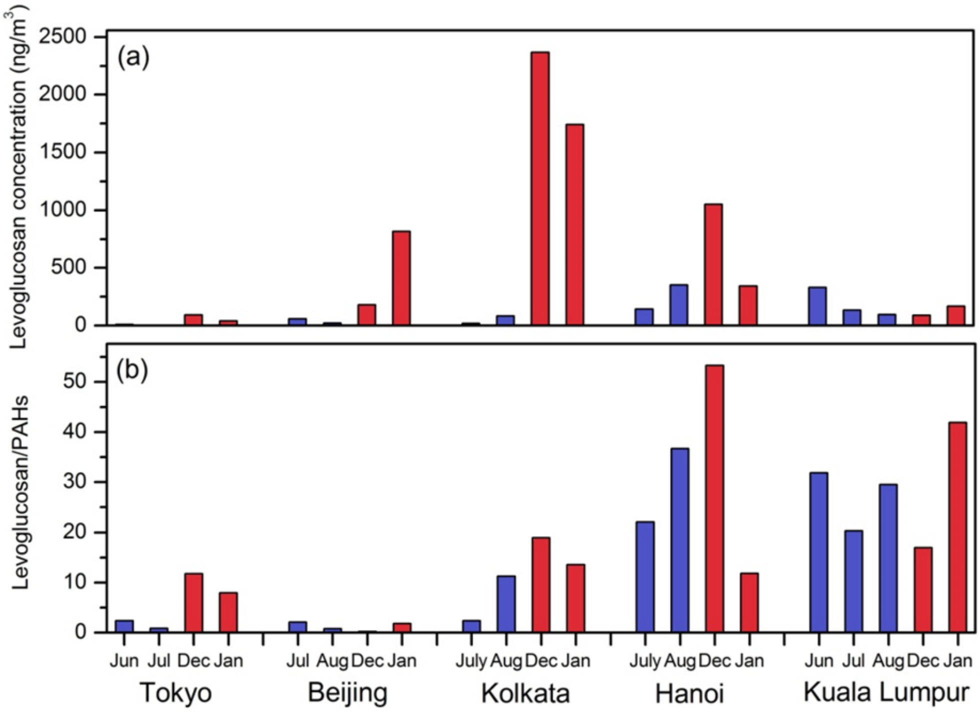

Fig. 7. Seasonal variations in levoglucosan concentration and levoglucosan/PAHs ratio in aerosol samples of five metropolitan cities of Asia. *(The blue and red points are indicating the value in non-winter and winter season respectively).*

winter suggested high biomass combustion. The highest concentration was seen in Kolkata, consistent with high biomass burning there (Chowdhury *et al.*, 2007). Concentrations were high in Beijing and Hanoi but low in Tokyo. High concentrations detected previously in Kuala Lumpur point to biomass burning during haze episodes (Abas *et al.*, 2004), which are commonly due to wildfires and biomass burning in Malaysia during the dry season (May–September) (Abas *et al.*, 2004), along with the contribution of vehicle emissions (Abas *et al.*, 1996). Previous studies have found changes in the concentrations and composition of PAHs in the air of Malaysian cities during haze episodes (Abas *et al.*, 2004; Omar *et al.*, 2006), and attributed a high concentration of total PAHs (47.89 ± 0.09 ng m^{-3}) to biomass combustion (Abas *et al.*., 2004). Though levoglucosan concentrations in PM from Kuala Lumpur were moderate, its ratio to PAHs was consistent with Abas *et al.* (2004) as follows.

We also used levoglucosan/PAHs ratios to determine the contribution of biomass burning to total PAHs (Fig. 7(b)).

Although Kuala Lumpur had low ∑36 PAHs, it had a high contribution from biomass burning. In contrast, Beijing, with the highest ∑36 PAHs, had the lowest ratio, indicating a low biomass contribution. The biomass contribution was second highest in Hanoi and lowest in Tokyo followed by Kolkata.

Sources of PAHs in the Five Cities

In Beijing, coal combustion was a major source of PAHs, especially in winter, along with a constant contribution from vehicle exhaust throughout the year, consistent with the results of Coulibaly *et al.* (2016) and with higher levels of PAHs in Beijing than in other cities in China (Liu *et al.*, 2014, Liu *et al.*, 2015). Concentrations of PAHs decreased from 2003 to 2011 in response to a number of measures taken to curb air pollution in preparation for the Olympic Games in Beijing in 2008 (Zhou *et al.*, 2009; Ma *et al.*, 2011, Li *et al.*, 2013). In a recent study, the yearly average concentrations of PM_{10}, SO_2 and NO_2 decreased in Beijing from 2004 to 2010 (Tang *et al.*, 2017), suggest that source control measures executed by the city had a constructive effect on the Beijing air pollution. The measures may be included switching from coal to natural gas, traffic control, restricting construction work, and relocating or closing down heavily polluting industries. However, our measurements after the Games (i.e., Sep. 2009 to Aug. 2010) showed the major contribution of coal combustion to increasing concentrations of PAHs in the air in Beijing.

In Kolkata, coal combustion, vehicle exhaust, and wood burning contributed equally to PAHs, as supported by previous studies (Reddy *et al.*, 2002, Cheng *et al.*, 2013). Compared with other cities in India, Kolkata relies more on traditional industries (e.g., brick factories) than on light and high-tech industries. Rates of energy consumption suggest that coal combustion is highest in Kolkata (Garg *et al.*, 2001), which is explained by the presence of traditional industries and heavy industries. In addition, the use of wood and cow dung for cooking is prevalent in Kolkata. Estimates based on emission factors of diverse sources indicate that coal combustion in both cooking and heavy industry releases a high proportion of PAHs (Chakraborty *et al.*, 2010). Vehicle emissions were identified as a main source of PAHs in ambient air in Kolkata (Hussein *et al.*, 2016). Thus, coal and wood combustion and vehicle exhaust contribute equally to PAH emissions in Kolkata.

In Hanoi, vehicle-related emissions are a major source of PAHs (Tuyen *et al.*, 2014), with a significant contribution from wood burning. Motor bikes make up 90% of vehicles in Hanoi; most do not have catalytic convertors, and many are old and poorly maintained, contributing to increased emissions (Thuy *et al.*, 2012). Interestingly, our results support these findings. We also identified a small but significant contribution from wood burning.

In Kuala Lumpur, vehicles were a major source of PAHs; although forest-fire-(haze)-derived PAHs were predominant in the dry season, as also reported by Jamhari (2014).

In Tokyo, both vehicle exhaust and high-temperature combustion contributed to PAHs in PM. Vehicle exhaust contributed to lower-molecular-weight species such as phenanthrene, although a clear distinction from high-temperature combustion of coal was not achieved, possibly because little coal is burned for heating in downtown Tokyo, and vehicle emissions are strictly regulated. Japan's location downstream of China makes the influence of PAHs of concern (e.g., Yang *et al.*, 2007), but our measurements clearly showed no influence of long-range transport from China to Tokyo. Local sources contribute more in Tokyo. PM samples collected in 2001 at suburb site in Tokyo (Murakami *et al.*, 2012) showed similar range of PAHs (∑12 PAHs: 2.63 ± 2.27 ng m^{-3} on average from Jun. to Nov.) to our present observation (∑12 PAHs: 3.37 ± 1.07 ng m^{-3} on average from Jun. to Nov.) in 2010. Considering different site (suburb in 2001 vs. downtown in 2010), no temporal change in PAH level was observed in Tokyo from 2001 to 2010. Carcinogenic PAHs such as BaP was significantly detected. Further monitoring is necessary in future.

CONCLUSION

PAH concentrations increased in the order of Kuala Lumpur ≈ Tokyo < Hanoi << Kolkata << Beijing. The most abundant PAHs detected were Chry, BaA, benzofluoranthenes, BaP, and BeP. The total PAH concentrations varied seasonally, showing significant increases in Beijing, Kolkata, Hanoi, and Tokyo during winter and in Kuala Lumpur during the dry season. Low concentrations during summer in Beijing, Kolkata, Hanoi, and Tokyo might be due to heavy rainfall. Ratios of methylated PAHs to parent PAHs and the hopane composition showed that all cities except Beijing during winter had significant inputs of vehicle-generated PAHs. Higher abundance of β isomers (17β21β(H)-C_{30}hopane and 17β21β(H)-C_{29}hopane) in Beijing indicates heavy use of coal during the winter. Overall, biomass contributed more in Kuala Lumpur and Hanoi. Beijing had a greater contribution from coal combustion, which surges during winter. We can summarize sources of PAHs for individual cities as follows:

Beijing: Coal combustion is the major source of PAHs, especially in winter, along with consistent contribution of vehicle exhaust throughout the year.

Kolkata: Coal combustion, vehicle exhaust, and wood burning contribute equally.

Kuala Lumpur: The major source of PAHs is vehicles, although forest fires are predominant in the dry season.

Hanoi: The major source is vehicles, with a significant contribution from wood burning.

Tokyo: Vehicle exhaust contributes lower-molecular-weight species, and high-temperature combustion contributes high-molecular-weight species.

These results demonstrate the usefulness of molecular markers, including PAH composition, to identify sources of atmospheric PAHs. However, the compositions of individual markers in source materials are variable and site-specific. For more quantitative source discrimination, more detailed sampling and analysis of potential source materials should be conducted at individual sites and in different seasons.

Due to the rapid economic growth and associated increase in the emission of PAHs, there has been increasing number of researches on atmospheric PAHs in Asia. For concrete understanding of the temporal trend and assessment of the effectiveness of the regulations, periodic monitoring is important. Our data provide benchmark data, i.e., pollution status in ~early 21st century, for future measurement.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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