Seasonal and spatial trends of suspended-particle associated polycyclic aromatic hydrocarbons in urban Shizuoka, Japan

Kazunari Kume [a,b], Takeshi Ohura [a,*], Takahiro Noda [a], Takashi Amagai [a], Masahiro Fusaya [a,b]

[a] *Graduate School of Nutritional and Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan*
[b] *Shizuoka Institute of Environment and Hygiene, 4-27-2 Kita-ando, Shizuoka 420-8637, Japan*

Abstract

We characterized the monthly variations of 21 polycyclic aromatic hydrocarbons (PAHs) associated with suspended particles in the city of Shizuoka, Japan, over 12 months during 2001 and 2002. The fraction of fine particles (less than 2.5 μm diameter (PM2.5)) ranged from 40 to 60% of total suspended particles over the 12 months of the study, and their concentrations ranged from 19.3 to 41.7 μg/m^3. Almost all the PAHs were found in the PM2.5 fraction, in which the summed concentration ($\sum$PAH) of the 21 PAHs ranged from 1.0 to 8.4 ng/m^3. PAH concentrations were elevated in the colder seasons, but the concentrations of the PM2.5 fraction of suspended particles were not. The composition of PAHs associated with PM2.5 changed little during the year of our study, indicating that seasonal sources such as heating have little effect. Factor analysis showed that three factors explain little of the seasonal variations in the sources of PAHs. Contour maps showed high concentrations of indicator PAHs for gasoline and diesel engine sources distributed along major roads and near factories on the outskirts of the city. We concluded that the contribution of vehicle exhausts to particle-associated PAHs is significant not only in the central city, but also in outer areas associated with major ring roads, and suggest that air pollution in outskirts of urban area also is concerned for health risk associated with the exposure.
© 2006 Elsevier B.V. All rights reserved.

Keywords: PAH; PM2.5; Factor analysis; Emission source; Regional distribution

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), some of which are known to be mutagens, carcinogens, and toxics, are ubiquitous environmental pollutants [1]. Most PAHs emitted to the ambient air are formed during the incomplete combustion of organic material [2]; that is, anthropogenic activities such as industry, residential heating, power generation, and motor vehicle use become major sources of atmospheric PAHs associated with particulates. Depending on their individual chemical and physical properties, PAHs in the air can be present either in gaseous phase or adsorbed on particulate matter [3,4]. Although their distribution and phase may vary seasonally, less than 3-ring PAHs are mostly found in the gaseous phase, whereas those of higher molecular weight (more than 5-rings) are mainly associated with particles [3–6]. In particular, most carcinogenic PAHs have four or more rings, and are typically adsorbed on fine particles with a

diameter less than 2.5 μm (PM2.5 fraction). In addition, PM2.5 contains the toxic chemicals that can cause respiratory diseases, such as lung cancer, because their inhalation leads to deposition deeper in the lungs than is the case with coarser particles [7–9]. Accordingly, it is important to investigate the distribution and possible sources of PAHs associated with PM2.5 to allow an assessment of their possible impact on human health.

Sources, emitted amounts, gas/particulate partitioning coefficients of PAHs, atmospheric loss mechanisms such as long-range transport, and photolysis are potential factors affecting the seasonal variability of atmospheric PAHs. In addition, climatic conditions such as temperature and wind direction contribute to the seasonal variability of atmospheric PAHs [10–13]. Therefore, investigating the seasonal variability of such air pollutants would provide important clues to the sources and atmospheric behavior of these pollutants.

Recently, the proliferation of motor transport, rather than industrial activities, is advanced in political and/or commercial cities, it provides the main contribution to growing levels of pollution such as PAHs. A number of studies related to ambient PAHs in urban environments have been conducted in cities

---

around the world; however, many of these have been limited in their spatial and temporal sampling [10,11,14–17]. Therefore, it is difficult to extract accurate information on temporal variations, distributions, and exposure to air pollutants from these studies.

In our study we investigated the concentrations of suspended particles and associated PAHs in various particle-size fractions, once a month for a year, at 31 sites in the city of Shizuoka, Japan. The main objectives of our study were to: (1) characterize ambient particles and associated PAHs over 1 year by determining PAH concentrations in the fine (PM2.5) and coarse (PM2.5–10 and PM > 10) fractions; (2) enhance the accuracy of the identification of PAH emission sources by using factor analysis; (3) clarify the seasonal spatial trends and possible sources of particulate PAH distribution in Shizuoka.

2. Materials and methods

2.1. Sampling sites

Our study was carried out in the city of Shizuoka (latitude 35°09′N, longitude 138°42′E; Fig. 1) which has a temperate climate, about 700,000 inhabitants, and is typical of commercial cities in Japan. The wind is usually moderate throughout the year; mean wind speed is ca. 2.2 m/s. The total rainfall during the sampling year was 2131 mm and the annual mean temperature was 18.2 °C. There was no snowfall during the sampling period. The study area lies between ocean and mountains and is predominantly residential, mainly in the form of low-rise buildings. There are a few factories (e.g. a paper-making plant) in the southwestern part of the study area. National main roads carry heavy traffic through the city. Some traffic statistics for 1999 were: Route 1, ca. 47,000 vehicles/day, of which 11% were large diesel trucks; Route 1 bypass (1B), ca. 45,000 vehicles/day in 1999, of which 33% were large diesel trucks; Route 150, ca. 48,000 vehicles/day, of which 16% were large diesel trucks; the Tomei Expressway, ca. 70,000 vehicles/day, of which 56% were large diesel trucks.

A total of 31 sampling sites were selected from within a 13 km × 13 km square including the center of the city (Fig. 1). The sampling sites were located as follows: 12 sites within 0.5 km of busy roads, 9 sites between 0.5 and 1 km from busy roads, and 10 sites more than 1 km distant from busy roads. Monitoring of particulate PAHs was conducted at each sampling site on one weekday per month during the period from February 2001 to January 2002. All the air samplings in 31 sampling sites were carried out in same day.

2.2. Air sampling

Particulate PAHs were collected and size-fractionated using a personal cascade impact (PCI) sampler (Tokyo Dyrec, Tokyo, Japan) combined with an MP-603 mini-pump (Sibata Scientific Technology Ltd., Tokyo, Japan). The PCI sampler consisted
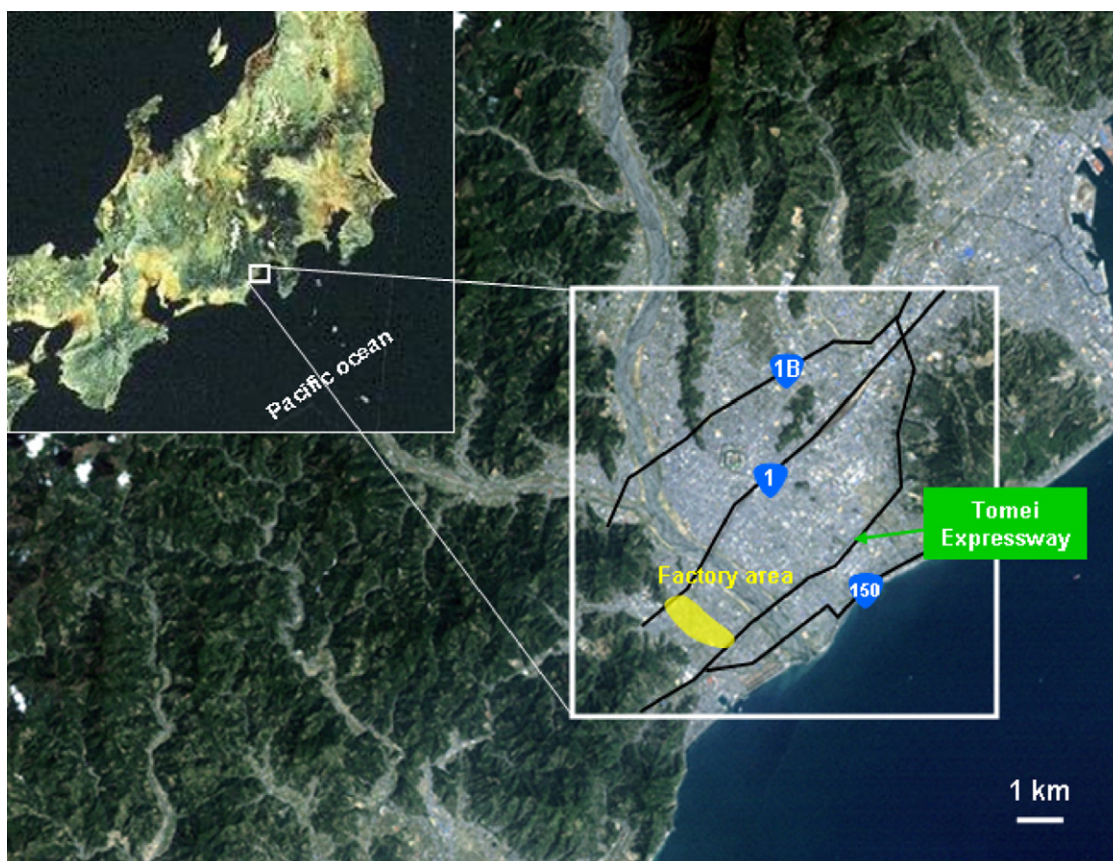

Fig. 1. Location of study area.

of three stages with a round 47-mm diameter Teflon fiber filter (TK15-G3M, Gelman Pallfex, Tokyo Dyrec, Tokyo, Japan). Airborne particles were size-fractionated based on their aerodynamic diameter at each of three stages: below 2.5 μm (PM2.5), 2.5–10 μm (PM2.5–10), and above 10 μm (PM > 10). The flow rate was 3.0 L/min and the duration of each sample was 24 h. The sampling equipment was placed externally on the second floor of selected buildings in the study area and separated from the wall by at least 2 m to prevent aspiration of dust from the building structure. Before and after sampling, the filters were kept in a desiccator under constant temperature and 50% relative humidity for at least 24 h. The filters were weighed with an electronic balance of 1-μg sensitivity (M5P-F, Sartorius Japan, Tokyo, Japan) and stored at −80 °C until samples were extracted.

2.3. Target PAHs and reagents

The target compounds for this study were 21 species of 3- to 7-ring PAHs. The compounds monitored in this study were: fluoranthene (Fluor), pyrene (Py), 1-methylpyrene (1MP), chrysene (Chry), triphenylene (Tph), benz[*a*]anthracene (BaA), *p*-terphenyl (pTer), perylene (Pery), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*j*]fluoranthene (BjF), indeno[1,2,3-*cd*]pyrene (IP), benzo[*ghi*]perylene (BghiP), benzo[*b*]chrysene (BbC), picene (Pi), dibenz[*a,c*]anthracene (DBacA), dibenz[*a,h*]anthracene (DBahA), coronene (Cor), and dibenzo[*a,e*]pyrene (DBaeP).

The PAH standard reagents were of the highest purity available and were dissolved in acetonitrile (Wako Chemicals, Osaka, Japan). The standard solution of the 21 PAHs (3- to 7- ring PAHs) was prepared by combining the individual PAH stock solutions. The dichloromethane used for extraction was residual-pesticide-analysis grade (Wako Chemicals, Osaka, Japan), the dimethylsulfoxide (DMSO) used for sample preparation was fluorometric-analysis grade (Dojindo Chemical Corp., Kumamoto, Japan), and the methanol and distilled water for the mobile phase were HPLC grade (Wako Chemicals, Osaka, Japan).

2.4. PAH analysis

Particulate PAHs were extracted with 10 ml dichloromethane in an ultrasonic bath for 20 min. After centrifugation at 3000 rpm for 10 min, a known volume (5–9 ml) of extract was transferred to another test tube. Fifty microliters of DMSO was then added to preserve the PAHs, and the dichloromethane solvent was evaporated under N_2. The residues were then dissolved in 950 μL of acetonitrile, and the target PAHs were analyzed by liquid chromatography with fluorescence detection.

The PAHs were separated in an HPLC system consisting of an L-6000 series pump, an L-5090 degasser, an AS-2000 auto-sampler, an F-1080 spectrofluorometer (Hitachi Corp., Tokyo, Japan), a mixer (Agilent Technologies, Palo Alto, CA), a CO630 column oven, and a six-way valve (GL Science Corp., Tokyo Japan). The pre-column (internal diameter 4.6 mm, length 30 mm) for PAH condensation and cleanup and the main column

(internal diameter 4.6 mm, length 250 mm) for separation were Wakosil-II 5C-18 PAH (Wako Chemicals, Osaka, Japan). PAHs were detected by two spectrofluorometers connected in series, with detection wavelengths automatically varying during analysis. A sample solution (40–300 μL) was injected into the HPLC system by the auto-sampler. The HPLC analytical conditions were as described by Ohura et al. [18].

The detection limits for individual PAHs, defined as triple the standard deviation of the peak height of a dilute standard solution, ranged from 0.37 pg (BkF) to 3.6 pg (Cor). We previously evaluated the accuracy and precision of this method by comparing the concentrations of certain PAHs associated with particles obtained from the cascade impactors and the tapered element oscillating microbalance (TEOM) monitor [19]. The ratios of PAH concentrations determined with PCI samplers and TEOM monitor was $101.1 \pm 6.9\%$, indicating that the analyses of our present study were reliable [19].

2.5. Quality assurance

To guarantee an unbiased analysis, field blank samples (clean glass fiber filter) at 5 sampling locations, and duplicate samples at 10 sampling locations, were analyzed. Field blanks were placed unopened next to the samplers for the duration of sampling, after which they were returned to the laboratory and treated as regular samples. When the blank samples were analyzed, none of the 21 target PAHs were detected. Differences between duplicate samples were less than 20%.

2.6. Data analysis

To determine the sources of PAHs, using compositional analysis, we performed factor analysis (FA) on the concentrations of individual PAHs corresponding to the 31 sampling sites in the seasonal data sets of February, May, August, and November. Here, we selected PAHs in the PM2.5 fraction for the analysis because the particle-associated PAHs were predominantly in this fraction throughout the year. The purpose of this statistical analysis was to (1) characterize sites and (2) identify the sources and processes that affected PAH concentrations. We performed FA by using statistical analysis software (SSRI Co. Ltd., Tokyo, Japan). Contour maps were constructed using spatial analyst software; Gsharp version 2.0 (Japan Information Processing Service Co. Ltd., Tokyo, Japan). Contour maps were created from the raw concentrations of PAHs associated with PM2.5. A bilinear interpolation algorithm was used to contour the scattered data, and the boundary condition used for mapping was the minimum PAH concentration obtained.

3. Results and discussion

3.1. Concentrations of size-fractionated particles and associated PAHs

The monthly individual geometric mean concentrations of size-fractionated particles and of the associated PAHs collected at the 31 sampling sites in the city are listed in Table 1. The

Table 1
Geometric mean concentrations of fractionated particle matter (PM, μg/m³) and individual PAHs (ng/m³) sampled monthly between February 2001 and January 2002 at 31 sampling sites in urban Shizuoka, Japan

	02/01	03/01	04/01	05/01	06/01	07/01	08/01	09/01	10/01	11/01	12/01	01/02
PM												
>10 μm	15.4	11.8	18.5	11.2	21.3	17.2	13.0	15.9	10.4	11.3	8.2	10.8
2.5–10 μm	18.5	18.9	35.3	12.3	20.6	18.1	20.7	16.3	12.5	9.4	13.0	13.2
<2.5 μm	38.9	40.5	38.1	30.1	27.9	34.6	36.7	36.2	25.8	18.7	20.7	26.7
PAH												
Fluor	0.231	0.196	0.223	0.097	0.077	0.062	0.125	0.043	0.179	0.386	0.149	0.220
Py	0.188	0.161	0.289	0.089	0.038	0.048	0.084	0.039	0.157	0.459	0.104	0.192
1MP	0.006	0.004	0.006	0.003	0.002	0.002	0.002	0.002	0.005	0.011	0.005	0.005
Chry	0.364	0.197	0.520	0.190	0.120	0.112	0.145	0.052	0.289	0.855	0.383	0.296
Tph	0.113	0.060	0.100	0.035	0.029	0.017	0.016	0.014	0.085	0.123	0.079	0.090
BaA	0.148	0.108	0.137	0.050	0.050	0.054	0.058	0.027	0.116	0.403	0.229	0.147
pTer	0.044	0.037	0.061	0.022	0.013	0.017	0.017	0.006	0.025	0.057	0.057	0.039
Pery	0.056	0.061	0.061	0.022	0.029	0.033	0.029	0.015	0.057	0.112	0.145	0.104
BeP	0.699	0.326	0.521	0.173	0.200	0.203	0.211	0.100	0.435	0.635	0.843	0.617
BaP	0.479	0.367	0.439	0.179	0.185	0.179	0.193	0.080	0.367	0.710	0.903	0.621
BbF	1.025	0.443	0.807	0.257	0.266	0.282	0.311	0.122	0.637	1.095	1.191	0.880
BkF	0.347	0.187	0.270	0.095	0.104	0.075	0.068	0.039	0.192	0.400	0.424	0.281
BjF	0.430	0.299	0.374	0.126	0.158	0.161	0.161	0.074	0.359	0.658	0.744	0.557
IP	0.830	0.430	0.636	0.180	0.268	0.212	0.244	0.156	0.565	0.929	1.141	0.748
BghiP	0.774	0.439	0.590	0.228	0.252	0.154	0.214	0.162	0.535	0.742	1.131	1.042
BbC	0.047	0.031	0.033	0.010	0.015	0.015	0.011	0.008	0.027	0.060	0.072	0.062
Pi	0.184	0.079	0.152	0.039	0.065	0.055	0.070	0.035	0.122	0.208	0.185	0.160
DBacA	0.039	0.028	0.040	0.015	0.022	0.045	0.058	0.019	0.042	0.073	0.084	0.085
DBahA	0.082	0.036	0.048	0.016	0.023	0.018	0.021	0.014	0.043	0.064	0.081	0.072
Cor	0.306	0.209	0.217	0.080	0.112	0.073	0.087	0.069	0.235	0.394	0.408	0.367
DBaeP	0.153	0.072	0.130	0.033	0.047	0.042	0.038	0.022	0.092	0.196	0.200	0.103

seasonal variability of size-fractionated particle concentrations, and PAH concentrations and composition is illustrated in Fig. 2.

Air temperatures during sampling ranged from 5.5 to 29.4 °C (annual mean, 18.2 °C), and are indicative of the relatively mild climate of the city of Shizuoka (Fig. 2). Total concentrations of suspended particles (TSP) ranged from 39.3 μg/m³ in November to 91.8 μg/m³ in April, and were relatively higher in February to April and June to September (Fig. 2). The concentrations of
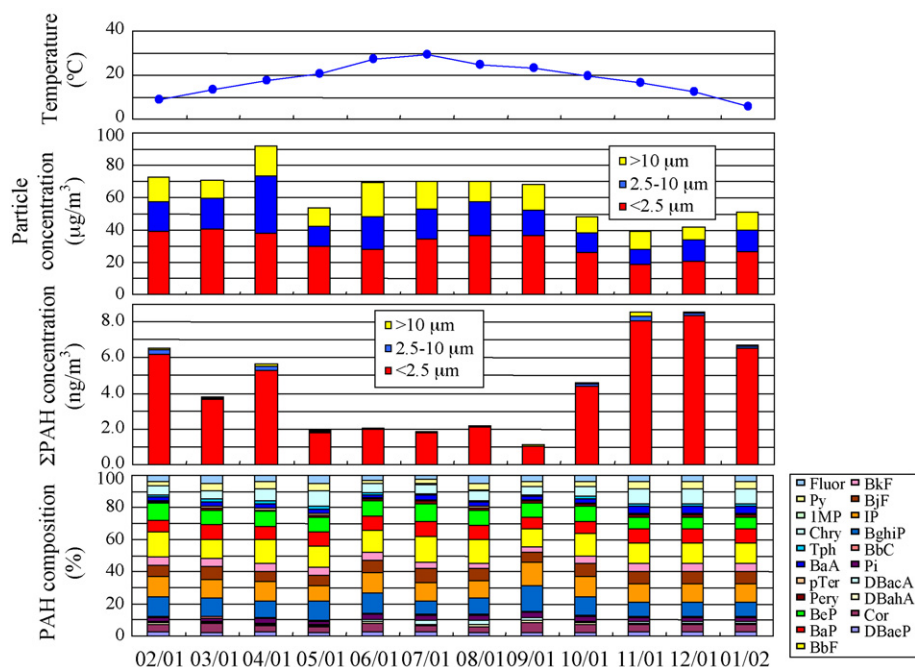

Fig. 2. Monthly variations of (a) temperature, (b) geometric mean concentrations of size-fractionated particles, (c) total concentration of PAHs ($\sum$PAH), and (d) composition of PAHs.

PM2.5 ranged from 18.7 µg/m^3 in November to 40.5 µg/m^3 in March, and this fraction accounted for 40–56% of TSP during the study period (Fig. 2). Hien et al. [20] reported that the distribution of particles between the fine and the coarse mode was strongly dependent upon meteorological conditions, such as wind speed, air temperature, and relative humidity. Some researchers have also reported that the size distribution follows seasonal trends [21]. However, in this study, there were no significant correlations between temperature and either the level or the composition of TSP in this study (data not shown).

The annual mean concentration of PM2.5 was 31.2 µg/m^3, which is more than double the limit (15 µg/m^3) regulated in the United States [22]. The mean concentration of PM2.5 at Shizuoka was also higher than that of some European cities in countries including Germany (13.8 µg/m^3), Netherlands (18.3 µg/m^3), and Sweden (10.3 µg/m^3) [23]. The range of concentrations for the PM2.5–10 and PM > 10 fractions at Shizuoka were 9.4–35.3 µg/m^3 and 8.2–21.3 µg/m^3, respectively, and the proportions of TSP for each fraction were 23–38% and 18–31%, respectively.

Twenty-one PAHs were detected in each of the three fractions we measured. The total PAH concentration ($\sum$PAH) ranged from 1.10 ng/m^3 in September to 8.57 ng/m^3 in November, and was relatively higher in autumn and winter (November–February) than that in spring and summer (May–September) (Fig. 2). The concentrations of $\sum$PAH associated with the PM2.5 fraction ranged from 1.02 ng/m^3 in September to 8.41 ng/m^3 in December. The PM2.5 fraction accounted for 94–98% of $\sum$PAH during the study period, which indicates that almost all PAHs are associated with the PM2.5 fraction throughout the year (Fig. 2). The $\sum$PAH concentrations associated with PM2.5 showed a significant negative correlation with temperature ($P < 0.01$, t-test).

Ambient PAH concentrations have been known to be generally higher during the winter season and lower during the summer season [10,11,13,14–18]. Seasonal activities such as the use of fossil fuels for heating in winter, and photo-decay reactions of ambient PAHs in the summer, are believed to be the main causes of seasonal variations. Moreover, it is recognized that meteorological effects, such as wind direction (e.g. southerly summer sea breezes carrying little pollution) can affect pollution levels. If seasonal sources such as fossil fuels are dominant ones for particulate PAHs in this sampling area, the PAH composition could different in each season. However, there was no significant difference in the PAH composition during the period of our investigation, whereas a seasonal trend of PAH concentrations was observed (Fig. 2). This fact suggested that the ambient PAHs could be affected by vehicles and stationary source which were a little seasonal difference. In the following sections, we aim to elicit these sources using compositional, statistical, and spatial distribution analysis.

3.2. Compositional analysis of PAHs

Particular PAH concentrations and PAH composition ratios can be used as tracers to distinguish among diverse potential sources. Some researchers have consistently used diagnostic

PAH composition ratios to help them identify possible emission sources [24–27]. Kulkarni and Venkataraman [28] identified PAH tracers for several urban sources: phenanthrene (Phe), Py, and Fluor for incineration processes; BaP and Fluor for wood combustion; BghiP and IP for gasoline fuels; Fluor and Py for heavy-duty diesel fuels. To characterize the PAH emission sources in our study, we calculated the ratios of specific PAHs in our data using PAHs such as BaA, Chry, BeP, BaP, IP, and BghiP. The calculated seasonal values of these ratios and their corresponding sources are presented in Table 2 with a comparison of our results with results from similar studies in countries other than Japan.

The concentrations of BaP recorded in Shizuoka were lower than most of those reported from other cities and the seasonal variations in PAH ratios from Shizuoka were small (Table 2). The ratios BaA/Chry, BaP/(BaP + Chry) and IP/(IP + BghiP) from Shizuoka were similar to those from other cities. On the other hand, BaP/BghiP ratios from Shizuoka were higher than those from other cities except Seoul and BeP/BaP ratios from Shizuoka were lower than those from other cities [10,26,27,29–32]. The annual means of the ratios BaP/BghiP and IP/(IP + BghiP) from Shizuoka were 0.78 and 0.51, respectively, indicating that diesel engines rather than gasoline engines were the dominant source of PAHs [33–36]. On the other hand, the annual mean ratios BaA/Chry, BeP/BaP, and BaP/(BaP + Chry) were 0.43, 1.09, and 0.58, respectively, indicating that gasoline engines were the dominant source of PAHs [33–36]. None of the calculated ratios indicated a significant contribution of PAHs from wood fires, incinerators, or oil-burning power plant sources [36]. Consequently, the compositional analysis showed that vehicle exhaust was the main contributor to suspended particle-associated PAHs in Shizuoka.

3.3. Factor analysis of PAHs

We used factor analysis (FA) to increase the confidence in our identification of emission sources. The principle of FA is to transform an original set of variables into a smaller set of linear combinations that account for most of the variance of the original set. The factor loadings which are obtained for each variable within the factors generated by the FA, are a type of correlation coefficient, and higher values are therefore associated with greater significance. Factor analysis has been widely used to investigate similarities and differences in the behavior of the concentrations of ambient PAHs [27,37–39].

The concentrations of 21 PAH species measured at the Shizuoka study site were subjected to FA with varimax rotation. Table 3 provides the results of FA for PAH concentrations recorded in winter, spring, summer, and autumn. The FA results show that three factors explain most of the data variance. Factor 1 in winter, spring, and autumn, and factor 2 in summer, had a high factor loading for BaP, IP, BghiP, BbC, and Cor, which are mainly the multi-ringed, heavy molecular weight PAHs. Gasoline engine emissions have been identified as the source of these compounds [40,41]. Factor 2 in winter and spring, and factor 3 in summer, had high factor loadings for light molecular weight PAHs Chry and Tph, and heavy molecular weight PAHs BeP,

Table 2
Comparison of PM2.5 concentrations ($\mu g/m^3$), BaP concentrations associated with PM2.5 (ng/m^3), and PAH ratios from this study with those from similar studies in other countries

City	Sampling season	Location	Dominant source	PM2.5	BaP	BaA/Chry	BeP/BaP	BaP/BghiP	IP/(IP + BghiP)	BaP/(BaP + Chry)	Reference
Shizuoka, Japan	Annual mean	Urban	Traffic + stationary source	31.2	0.39	0.43	1.09	0.78	0.51	0.58	This study
	Winter (February 2001)			38.9	0.48	0.40	1.45	0.62	0.52	0.57	This study
	Spring (May 2001)			30.1	0.18	0.26	0.97	0.78	0.44	0.48	This study
	Summer (August 2001)			36.7	0.19	0.40	1.09	0.90	0.53	0.57	This study
	Autumn (November 2001)			18.7	0.71	0.47	0.89	0.96	0.56	0.45	This study
Seoul, South Korea	March–December 1993	Urban	Traffic		1.17	0.44	1.39	1.41	0.49	0.31	[10]
Copenhagen, Denmark	Winter 1996	Urban	Traffic		2.2		1.41	0.43			[29]
Sao Paulo, Brazil	May-July 2002	Urban	Traffic + stationary source	11.9	0.52	0.95	1.11	0.25	0.47		[27]
Birmingham, UK	Summer & winter 1992	Suburban	Traffic		0.23–0.73	0.62–0.67		0.30–0.38	0.36–0.51		[30]
Chapel Hill, USA	Winter 2002/2003	Suburban	Traffic		0.087	0.5	2.41	0.46	0.47	0.33	[31]
Naples, Italy	Sep. 1997	Industrial	Traffic		1.38	0.5	4.31	0.24	0.43	0.33	[26]
La Plata, Argentina	Summer & winter 1999/2002	Industrial	Petrochemical plants		0.75	0.85		0.49	0.42	0.46	[32]
			Gasoline			0.28–1.2[a]	1.1–1.3[a]	1.27[b]	0.18[c]	0.49[d]	
			Diesel			0.17–0.36[a]	2.0–2.5[a]	0.46–0.81[a]	>0.3[c]	0.73[d]	
			Firewood fire			0.93[a]	0.44[a]				
			Incinerators					0.14–0.6[a]			
			Oil-burning power plant					>2[a]			

[a] Data from Simcik et al. [36].
[b] Data from Masclet et al. [33].
[c] Data from Kavouras et al. [35].
[d] Data from Khalili et al. [34].

Table 3
Factor analysis of seasonal concentrations of PAHs associated with PM2.5 in Shizuoka, Japan

PAH	Winter (February)			Spring (May)			Summer (August)			Autumn (November)	
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2
Fluor	0.515		0.677			0.932	0.548				0.939
Py	0.566		0.649			0.813	0.743				0.932
1MP		0.778			0.904		0.939				0.788
Chry		0.810				0.940	0.770		0.548		
Tph		0.802			0.878		0.686		0.540		0.794
BaA		0.843			0.917		0.920			0.722	0.621
pTer			0.672				0.813				
Pery	0.557			0.759	0.543		0.624	0.654		0.906	
BeP	0.580	0.553	0.566	0.545	0.816		0.504		0.763	0.804	0.504
BaP	0.739	0.584		0.523	0.777			0.773		0.918	
BbF	0.557	0.582	0.559	0.549	0.804				0.769	0.884	
BkF	0.600	0.612		0.523	0.832				0.681	0.922	
BjF	0.629	0.609		0.647	0.654		0.560	0.658		0.961	
IP	0.757			0.933				0.926		0.964	
BghiP	0.741			0.639	0.673			0.709		0.915	
BbC	0.861			0.943				0.833		0.928	
Pi	0.749		0.573	0.977						0.890	
DBacA	0.776			0.752	0.561				0.656	0.738	
DBahA	0.760			0.576	0.652			0.770		0.867	
Cor	0.714			0.949				0.747		0.783	
DBaeP	0.795			0.945						0.853	
Initial eigen values	8.37	6.41	4.73	8.23	7.47	2.67	6.15	5.66	3.71	12.03	4.90
% of variance	39.87	30.58	22.55	39.19	35.57	12.76	29.30	27.00	12.70	57.30	27.30
Cumulative %	39.87	70.45	92.99	39.19	74.77	87.53	29.30	56.30	74.00	57.30	80.60
Source	Gasoline	Factories	Diesel	Gasoline	Factories	Diesel	Diesel	Gasoline	Factories	Gasoline	Diesel

Only factors with eigenvalue > 1.0, and factor loading >0.5 are included.

BbF, and BkF. Local sources, such as factories, have been identified as the main contributors of these PAHs [28,38,42] and their presence has been attributed to a stationary source. Factor 3 in winter and spring, factor 1 in summer, and factor 2 in autumn had high factor loadings for Fluor and Py, which are light molecular weight PAHs. These compounds have been identified as coming from diesel emission sources [40,41]. The results of FA agree with our compositional analysis in supporting vehicle exhaust emissions as the dominant source of PAH emissions in Shizuoka.

3.4. Spatial distribution of PAHs

When the relative magnitudes of air pollutant concentrations are displayed on a map, the local distribution of the pollutants becomes apparent, providing clues to the emission sources [13,43,44]. We constructed contour maps of the study area showing the seasonal magnitudes of PAH indicators for a gasoline engine source (Fluor and Py) and for a diesel engine source (BaP and BghiP), and considered them taking into account the wind directions (Fig. 3).

During winter sampling, the wind was blowing mainly from the northeast and the areas of high concentrations of light molecular weight PAHs, Fluor and Py, were distributed along the major road (Route 1B) in the northern area and near factories in western and southern areas. The highly polluted areas for heavy molecular weight PAHs, BaP and BghiP, were generally consistent with those for Fluor and Py. That is, the highly polluted areas were spread along the busy roads of the outer city, with an enclosed area of lower pollution in the central city.

In spring and summer, concentrations of all four indicator PAHs were low, but there were relatively high concentrations in the center of the study area. The wind directions in spring and summer were mixed with northwesterly and southerly to southeasterly winds predominant. Taking wind direction into account, both the summer and spring distributions of PAHs can be attributed to traffic on major roads and to factories in the west and south.

Distributions of the four indicator PAHs in autumn were interesting in that a similar enclosed area of lower concentrations to that observed in the central city area in winter was apparent, but shifted to the north. The higher concentrations of light molecular weight PAHs in autumn were distributed along the coastal area, and over a northwest to southeast expressway and other major roads (Route 150) crossing the study area from northeast to southwest. Wind directions varied in autumn, with northwesterlies and southeasterlies predominant (Fig. 3). This suggests that the differences in the observed distribution of highly polluted areas in winter and autumn might be due to the differences in seasonal wind directions. In addition, although the possible sources of PAHs, diesel and gasoline exhaust, in autumn might be expected to be much the same as those in winter, the contour maps give conclusive evidence of marked differences.
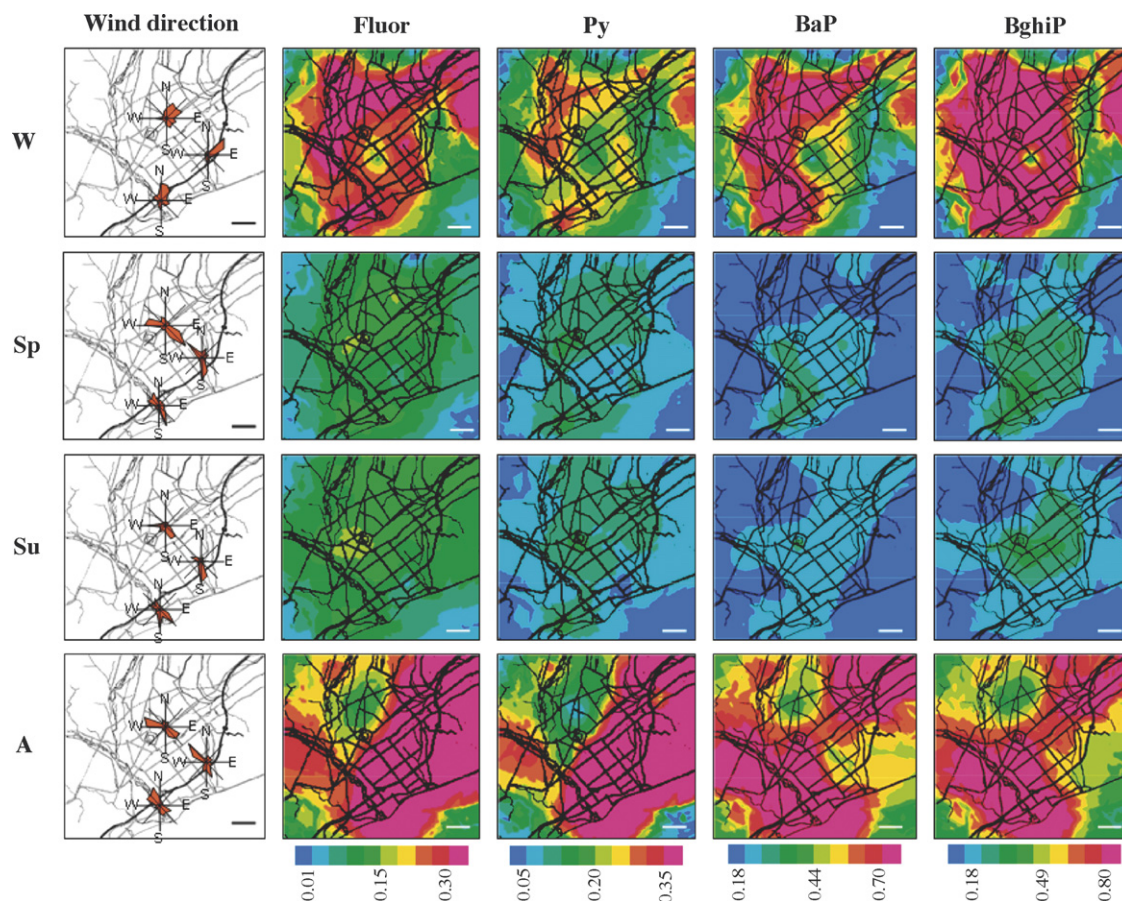
Fig. 3. Wind direction and contour maps of concentrations (ng/m^3) of selected PAHs (Fluor, fluoranthene; Py, pyrene; BaP, benzo[*a*]pyrene; BghiP, benzo[*ghi*]perylene) in winter (February), spring (May), summer (August), and autumn (November). Scale bar = 2 km.

4. Conclusions

TSP was relatively higher in spring and summer than during the remainder of the year. No seasonal trends of the levels and the proportion of the different size fractions were observed in our study. Twenty-one PAHs were detected in each fraction of the size-fractionated particles. There was a general trend for total concentrations of ambient PAHs ($\sum$PAH) to be relatively higher in the colder seasons than in the warmer seasons. A lack of variation of PAH compositions over a year might be evidence that seasonal effects on PAH concentrations are small, suggesting that traffic exhaust and industrial activities are the dominant sources of PAHs in the area because those activities are not influenced by the seasons. Both compositional analysis and factor analysis of seasonal PAH concentrations supported the view that vehicle exhaust is the dominant source of PAHs in Shizuoka. Contour maps of the concentrations of ambient PAHs revealed that highly polluted air was distributed along major roads outside the city center, and PAH concentrations were higher there than in the central city, although there were some differences in the distribution owing to variable seasonal wind directions. This pattern may be observed in other mega-urban cities where the entry of cars to the city center is limited. We concluded that traffic on highways around the perimeter of a city are potent sources of ambient PAHs and create more serious air pollution problems than those of the central city.

References

[1] B.J. Finlayson-Pitts, J.N. Pitts Jr., Chemistry of the Upper and Lower Atmosphere, Academic Press, San Diego, 2000.
[2] H. Richter, J.B. Howard, Formation of polycyclic aromatic hydrocarbons and their growth to soot-a review of chemical reaction pathways, Prog. Energy Combust. Sci. 26 (2000) 565–608.
[3] T.F. Bidleman, Atmospheric processes. Wet and dry deposition of organic compounds are controlled by their vapor-particle partitioning, Environ. Sci. Technol. 22 (1988) 361–367.
[4] M.P. Ligocki, J.F. Pankow, Measurements of the gas/particle distributions of atmospheric organic compounds, Environ. Sci. Technol. 23 (1989) 75–83.
[5] S.O. Baek, M.E. Goldstone, P.W.W. Kirk, J.N. Lester, R. Perry, Phase distribution and particle size dependency of polycyclic aromatic hydrocarbons in the urban atmosphere, Chemosphere 22 (1991) 503–520.
[6] T. Ohura, T. Sugiyama, T. Amagai, M. Fusaya, H. Matsushita, Simultaneous liquid chromatographic determination of 39 polycyclic aromatic hydrocar-

bons in indoor and outdoor air and application to a survey on indoor air pollution in Fuji, Japan, J. AOAC Int. 85 (2002) 188–202.

[7] C.A. Pope III, D.V. Bates, M.E. Raizenne, Health effects of particulate air pollution: time for reassessment? Environ. Health Perspect. 103 (1995) 472–480.

[8] C.A. Pope III, M.J. Thun, M.M. Namboodiri, D.W. Dockery, J.S. Evans, F.E. Speizer, C.W. Heath Jr., Particulate air pollution as predictor of mortality in a prospective study of U.S. adults, Am. J. Resp. Crit. Care Med. 151 (1995) 669–674.

[9] J. Schwartz, L.M. Neas, Fine particles are more strongly associated than coarse particles with acute respiratory health effects in schoolchildren, Epidemiology 11 (2000) 6–10.

[10] B.C. Panther, M.A. Hooper, N.J. Tapper, A comparison of air particulate matter and associated polycyclic aromatic hydrocarbons in some tropical and temperate urban environments, Atmos. Environ. 33 (1999) 4087–4099.

[11] M. Dimashki, L.H. Lim, R.M. Harrison, S. Harrad, Temporal trends, temperature dependence, and relative reactivity of atmospheric polycyclic aromatic hydrocarbons, Environ. Sci. Technol. 35 (1999) 2264–2267.

[12] A. Montelay-Massei, D. Ollivon, B. Garban, M. Chevreuil, Polycyclic aromatic hydrocarbons in bulk deposition at a suburban site: assessment by principal component analysis of the influence of meteorological parameters, Atmos. Environ. 37 (2003) 3135–3146.

[13] T. Ohura, T. Amagai, M. Fusaya, H. Matsushita, Spatial distributions and profile of atmospheric polycyclic aromatic hydrocarbons in two industrial cities in Japan, Environ. Sci. Technol. 38 (2004) 49–55.

[14] J.S. Park, T.L. Wade, S. Sweet, Atmospheric distribution of polycyclic aromatic hydrocarbons and deposition to Galveston Bay, Texas, USA, Atmos. Environ. 35 (2001) 3241–3249.

[15] S.Y. Bae, S.M. Yi, Y.P. Kim, Temporal and spatial variation of the particle size distribution of PAHs and their dry deposition fluxes in Korea, Atmos. Environ. 36 (2002) 5491–5500.

[16] P. Tsai, R. Hoenicke, D. Yee, Atmospheric concentrations and fluxes of organic compounds in the northern San Francisco Estuary, Environ. Sci. Technol. 36 (2002) 4741–4747.

[17] C. Schauer, R. Niessner, U. Poschl, Polycyclic aromatic hydrocarbons in urban air particulate matter: decadal and seasonal trends, chemical degradation, and sampling artifacts, Environ. Sci. Technol. 37 (2003) 2861–2868.

[18] T. Ohura, T. Amagai, M. Fusaya, H. Matsushita, Polycyclic aromatic hydrocarbons in indoor and outdoor environments and factors affecting their concentrations, Environ. Sci. Technol. 38 (2004) 77–83.

[19] T. Ohura, T. Amagai, T. Sugiyama, M. Fusaya, H. Matsushita, Characteristics of particle matter and associated polycyclic aromatic hydrocarbons in indoor and outdoor air in two cities in Shizuoka, Japan, Atmos. Environ. 38 (2004) 2045–2054.

[20] P.D. Hien, V.T. Bac, H.C. Tham, D.D. Nhan, L.D. Vinh, Influence of meteorological conditions on PM2.5-10 and PM2.5-10 concentrations during the monsoon season in Hanoi, Vietnam, Atmos. Environ. 36 (2002) 3473–3484.

[21] E. Manoli, D. Voutsa, C. Samara, Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece, Atmos. Environ. 36 (2002) 949–961.

[22] US EPA. National Ambient Air Quality Standards for Particulate Matter, Final Rule. Federal Register. 62 (138), Part II, EPA, 40 CFR Part 50, 18 July, 1997.

[23] J. Cyrys, J. Heinrich, G. Hoek, K. Meliefste, M. Lewne, U. Gehring, T. Bellander, P. Fischer, P.V. Vliet, M. Brauer, H.-E. Wichmann, B. Brunekreef, Comparison between different traffic-related particle indicators: elemental carbon (EC), PM2.5 mass, and absorbance, J. Expos. Anal. Environ. Epidemiol. 13 (2003) 134–143.

[24] C.K. Li, R.M. Kamens, The use of polycyclic aromatic hydrocarbons as source signatures in receptor modeling, Atmos. Environ. 27 (1993) 523–532.

[25] T. Nielsen, Traffic contribution of polycyclic aromatic hydrocarbons in the centre of a large city, Atmos. Environ. 30 (1996) 3481–3490.

[26] A.M. Caricchia, S. Chiavarini, M. Pezza, Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy), Atmos. Environ. 33 (1999) 3731–3738.

[27] C. Bourotte, M.C. Forti, S. Taniguchi, M.C. Bicego, P.A. Lotufo, A wintertime study of PAHs in fine and coarse aerosols in Sao Paulo city, Brazil, Atmos. Environ. 39 (2005) 3799–3811.

[28] P. Kulkarni, C. Venkataraman, Atmospheric polycyclic aromatic hydrocarbons in Mumbai, India, Atmos. Environ. 34 (2000) 2785–2790.

[29] T. Nielsen, A. Feilberg, M.L. Binderup, The variation of street air levels of PAH and other mutagenic PAC in relation to regulations of traffic emissions and the impact of atmospheric processes, Environ. Sci. Pollut. Res. 6 (1999) 133–137.

[30] R.M. Harrison, D.J.T. Smith, L. Luhana, Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K., Environ. Sci. Technol. 30 (1996) 825–832.

[31] J.D. Pleil, A.F. Vette, S.M. Rappaport, Assaying particle-bound polycyclic aromatic hydrocarbons from archived PM2.5 filters, J. Chromatogr. A 1033 (2004) 9–17.

[32] M. Rehwagen, A. Muller, L. Massolo, O. Herbarth, A. Ronco, Polycyclic aromatic hydrocarbons associated with particles in ambient air from urban and industrial areas, Sci. Total Environ. 348 (2005) 199–210.

[33] P. Masclet, M.A. Bresson, G. Mouvier, Polycyclic aromatic hydrocarbons emitted by power stations, and influence of combustion conditions, Fuel 66 (1987) 556–562.

[34] N.R. Khalili, P.A. Scheff, T.M. Holsen, PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions, Atmos. Environ. 29 (1995) 533–542.

[35] I.G. Kavouras, J. Lawrence, P. Koutrakis, E.G. Stephanou, P. Oyola, Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: source reconciliation and evaluation of sampling artifacts, Atmos. Environ. 33 (1999) 4977–4986.

[36] M.F. Simcik, S.J. Eisenreich, P.J. Lioy, Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan, Atmos. Environ. 33 (1999) 5071–5079.

[37] S.S. Park, Y.J. Kim, C.H. Kang, Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea, Atmos. Environ. 36 (2002) 2917–2924.

[38] G.C. Fang, Y.S. Wu, M.H. Chen, T.T. Ho, S.H. Huang, J.Y. Rau, Polycyclic aromatic hydrocarbons study in Taichung, Taiwan, during 2002–2003, Atmos. Environ. 38 (2004) 3385–3391.

[39] M. Kalaitzoglou, E. Terzi, C. Samara, Emission inventory and sources of polycyclic aromatic hydrocarbons in the atmosphere at a suburban area in Taiwan, Atmos. Environ. 38 (2004) 2545–2560.

[40] L.C. Marr, T.W. Kirchstetter, R.A. Harley, Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions, Environ. Sci. Technol. 33 (1999) 3091–3099.

[41] M.P. Fraser, M.J. Kleeman, J.J. Schauer, G.R. Gass, Modeling the atmospheric concentrations of individual gas-phase and particle-phase organic compounds, Environ. Sci. Technol. 34 (2000) 1302–1312.

[42] H.H. Yang, W.J. Lee, S.J. Chen, S.O. Lai, PAH emission from various industrial stacks, J. Hazard. Mater. 60 (1998) 159–174.

[43] T. Ohura, T. Amagai, M. Fusaya, Regional assessment of ambient volatile organic compounds in an industrial harbor area, Shizuoka, Japan, Atmos. Environ. 40 (2006) 238–248.

[44] K.H. Chiu, B.Z. Wu, C.C. Chang, U. Sree, J.G. Lo, Distribution of volatile organic compounds over a semiconductor industrial park in Taiwan, Atmos. Environ. 39 (2005) 973–983.