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Distribution, sources, and toxicity assessment of polycyclic aromatic hydrocarbons in surface soils of the Gwangju City, Korea

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ABSTRACT

Twenty-three individual polycyclic aromatic hydrocarbons (PAHs) including sixteen US Environmental Protection Agency (EPA) priority pollutants were analyzed in soil samples collected from twenty sites in the metropolitan city of Gwangju, Korea to investigate the levels of concentration, profiles, possible sources of PAHs, and a probabilistic human health risk. Soil samples (0–15 cm top layer) were collected, and the sampling sites were classified into two groups, including a school area and a residential area. Regardless of the sampling site, the concentrations of Σ_{23} PAHs ranged from 120 to 273 ng/g with an average value of 164 ng/g. The molecular distribution of PAHs reflected the similarity between school and residential areas in soil PAHs profile, and the PAHs could be from the same emission sources. High molecular weight PAHs (5- and 6-ring) were predominant in the soil samples, followed by 4-ring PAHs, while the fraction of 2-ring PAHs was the lowest. The total concentration of carcinogenic PAHs accounted for 54% of $\Sigma_{16\text{-EPA}}$ PAHs. Considering the different diagnostic ratios of PAHs, such as Flt/(Flt + Pyr), BaA/(BaA + Chr), Ant/(Ant + Phe), and IcdP/(IcdP + BghiP) and the principal component analysis results, the soil samples were likely attributed to mixed pyrogenic sources (coal and fossil fuel combustion, regardless of fuel types). The cancer risks for two age groups were $< 10^{-4}$, indicating no potential cancer risk.

1. Introduction

Over the last two decades, the rapid development of the economy has led to environmental contamination and pollution problems. Persistent organic pollutants (POPs), which cause adverse effects the environment and to human health, are ubiquitous and persistent in the environment, having long half-lives in soils, sediments, air or biota. Polycyclic aromatic hydrocarbons (PAHs) are a class of POPs and widespread contaminants in the environment (De La Torre-Roche et al., 2009; Larsen and Baker, 2003; Wang et al., 2011). Since the 70s, sixteen PAH compounds have been recommended as priority pollutants by US Environmental Protection Agency (EPA) as they have more carcinogenicity, mutagenicity, and toxicity than other PAHs, according to the International Agency for Research on Cancer (IARC) (IARC, 1987; Li et al., 2014). PAHs are primarily formed through the incomplete combustion of carbon containing fuels such as wood, coal, diesel, fat, and tobacco, and most sources of PAHs are anthropogenic, arising from industrial emissions, solid waste incineration, and vehicular emissions among others (Dong and Lee, 2009). Anthropogenic sources of PAHs can be separated into two groups, namely petrogenic and pyrogenic. Combustion of fossil fuels (coal and petroleum) and biomass generates pyrogenic PAHs, while petrogenic PAHs are defined as they originate from petroleum products, including kerosene, gasoline, diesel fuel, lubricating oil, and asphalt (Baek et al., 1991; Yunker et al., 2002). PAHs can contain more than two aromatic rings. Usually, PAHs with more than four rings are generally from pyrogenic sources (Dong and Lee, 2009; Zakaria et al., 2002).

In the last decade, a number of monitoring studies on PAH contamination have been conducted in various cities around the world and variability has been found in the total concentrations of PAHs (Albanese et al., 2014; Bandowe and Nkansah, 2016; Dong and Lee, 2009; Hussain et al., 2015; Liu et al., 2015; Melnyk et al., 2015; Nguyen et al., 2014; Pies et al., 2008; Yuan et al., 2014). Data concerning PAHs concentrations in the urban soil of Gwangju (South Korea) are not available. This lack of data has posed difficulties for pollution control and management. Therefore, this study evaluated the concentration levels, pattern, and emission sources of PAHs in the urban soil of the city.

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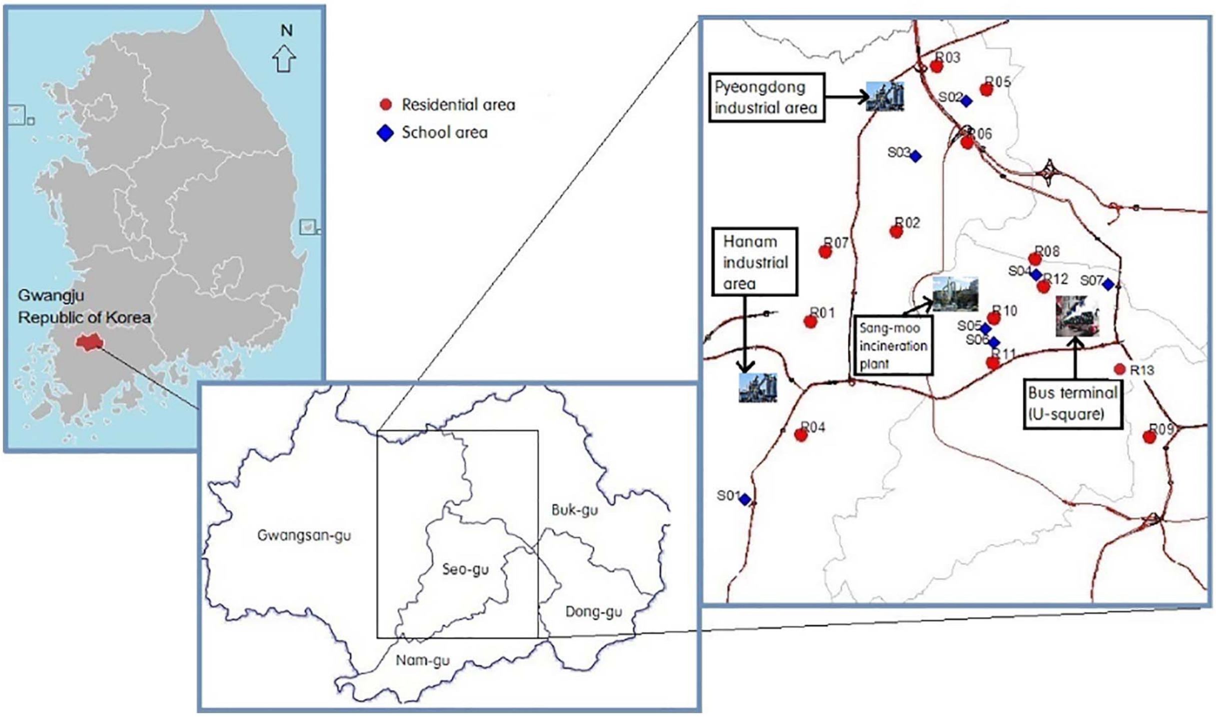

Fig. 1. Schematic map of sampling sites.

2. Materials and method

2.1. Study area and sampling

Gwangju is the sixth largest city in South Korea (latitude and longitude: 35°09′ to 35°10′ N, 126°38′ to 127°00′ E) and covers an area of approximately 501 km^2. The climate is characterized as having a hot and humid temperate monsoon season as well as dry and cold winters with a prevailing northwest wind. The average annual temperature range is 9.5–19.1 °C.

A total of 20 soil samples (0–15 cm top layer) were collected from the Gwangsan and Seo districts of Gwangju (Fig. 1) during April–June of 2013 and these sampling sites were selected since an industrial area, a bus terminal, and an incineration plant are found in these locations. The soil taxonomy among the 20 samples was classified into fine sand (10), loam fine sand (3), sandy loam (6), and loam (1). The sampling sites are classified into two groups, school areas and residential areas to identify the potential PAHs sources to those found in these areas and therefore examine the human health risks for PAH exposure to residential and school playground soil. Information on the collection sites of individual samples and the type of collected soil is presented in Table 1. At each sampling site, 3 to 5 sub-samples (100 g) were collected and mixed together. All the samples were collected using a stainless steel scoop and were kept in labeled glass bottles and directly stored in ice boxes to minimize the losses caused by volatilization. The soil samples were homogenized and sieved using a #10 mesh sieve ($<$ 2 mm) after removing stones and residual roots. Finally, composite samples were stored at $-$ 4 °C until instrumental analysis.

2.2. Sample analysis

The PAHs in each soil sample were measured via ultrasonic extraction (U.S. EPA 3550 method). Homogenized samples (15 g) were mixed with anhydrous sodium sulfate in a 250 mL glass beaker and four internal standards were added (300 μL) (d_8-naphthalene, d_{10}-phenanthrane, d_{12}-chrysene, and d_{12}-perlyne; 0.1 ppm). The soil samples were then extracted twice in each 100 mL solvent (n-hexane: acetone 1:1, v/v) for 3 min each cycle using ultra-sonication equipment (BRANSON, ultrasonic disruptor B-450, duty cycle 50%). The extracts were filtered using 5B filter paper and dehydrated when filtering through an anhydrous sodium sulfate. The extractants were then concentrated to 0.75 mL using a rotary evaporator (Biotage TurboVap® II). Aliquots were cleaned using 0.1 g silica gel to remove polar impurities. Finally, analysis of the PAHs in the supernatant was carried out using an Agilent 7890A gas chromatograph 5975C mass spectrometer (GC–MS, Agilent, USA). The temperature profile of the GC oven condition was as follows. The GC oven temperature was started at 50 °C. The temperature was then increased to 200 °C at 10 °C/min and held for 5 min. A new ramp of 20 °C/min was started until 310 °C, and was then held for 10 min. The inlet and detector temperatures were 285 and 300 °C, respectively. The injection of the 1 μL sample was conducted using an automatic sampler in splitless mode and helium was used as a carrier gas (2 mL/min). Analyte identification was confirmed by peak retention time in GC–MS and qualifier ions. The most abundant ion was chosen for quantification.

Twenty-three PAHs compounds including 16 US EPA priority pollutants were analyzed in all samples (Table 2). DBaeP and Cor co-eluted and were therefore quantified together. The internal standard, d_8-naphthalene was used to quantify the PAH with molecular weight ranging from Nap to Flu; d_{10}-phenanthrane was used for Phe to BaA, d_{12}-chrysene was used for Chr to BaP, and d_{12}-perlyne was used for Per to DBalP. The mean recovery percentages were 80.43%, 84.00%, 75.12%, and 77.84% for d_8-naphthalene, d_{10}-Phenanthrane, d_{12}-Chrysene, and d_{12}-Perlyne, respectively.

2.3. Source identification

2.3.1. PAH diagnostic ratios

One of the most common tools for identifying and assessing the appropriate pollution emission source is PAHs diagnostic ratios. The ratios are applicable to PAHs determined in different environmental media (Bucheli et al., 2004; Yunker et al., 2002). Among the different diagnostic ratios, BaP/BghiP, Flt/(Flt + Pyr), BaA/(BaA + Chr), Ant/(Ant + Phe), and Flu/(Flu + Pyr) are frequently applied to soil samples

Table 1
Information on soil samples collected.

Sample ID	Site	Location	SOM (wt%)	Type of soil
R01	Residential	35°09′23.57″ 126°47′40.20″	15.24	Sandy loam
R02	Residential	35°10′37.34″ 126°49′14.60″	1.85	Fine sand
R03	Residential	35°10′43.00″ 126°48′46.92″	2.17	Fine sand
R04	Residential	35°07′47.23″ 126°47′48.70″	9.73	Loam
R05	Residential	35°12′27.79″ 126°50′49.33″	7.91	Sandy loam
R06	Residential	35°11′56.85″ 126°50′27.44″	9.17	Sandy loam
R07	Residential	35°10′26.85″ 126°47′59.35″	7.40	Sandy loam
R08	Residential	35°10′17.29″ 126°51′29.95″	2.24	Fine sand
R09	Residential	35°07′49.03″ 126°53′46.20″	8.69	Sandy loam
R10	Residential	35°09′25.19″ 126°50′48.23″	3.89	Loam fine sand
R11	Residential	35°08′49.58″ 126°50′48.51″	2.13	Fine sand
R12	Residential	35°11′37.51″ 126°54′03.11″	3.04	Fine sand
R13	Residential	35°09′56.15″ 126°51′36.53″	3.34	Fine sand
S01	School	35°06′52.71″ 126°46′23.68″	6.54	Sandy loam
S02	School	35°12′38.11″ 126°50′18.94″	4.62	Loam fine sand
S03	School	35°11′49.79″ 126°49′27.79″	2.16	Loam fine sand
S04	School	35°10′08.65″ 126°51′35.91″	1.64	Fine sand
S05	School	35°09′19.73″ 126°50′40.54″	2.88	Fine sand
S06	School	35°09′09.06″ 126°50′49.20″	2.43	Fine sand
S07	School	35°10′00.00″ 126°52′47.55″	2.38	Loam fine sand
Max			15.24	
Min			1.64	
Mean			4.98	
Median			3.19	

SOM: soil organic matter.

for the identification of pollution emission sources (Yunker et al., 2002).

The ratio of Ant/(Ant + Phe) < 0.1 suggested a petroleum source, while a ratio of > 0.1 reflected combustion (Yunker et al., 2002). Meanwhile, Flt/(Flt + Pyr) < 0.4 indicated petroleum, between 0.4 and 0.5 implies liquid fossil fuel combustion, and a ratio of > 0.5 is the characteristic of biomass and coal combustion (Yunker et al., 2002). IcdP/(IcdP + BghiP) < 0.2 is an indication of petroleum sources, while that between 0.2 and 0.5 indicates that the PAHs usually derive from petroleum combustion (liquid fossil fuel, vehicle, and crude oil combustion) and IcdP/(IcdP + BghiP) > 0.5 strongly indicates the contribution of coal, grass, and wood (Tobiszewski and Namieśnik,

Table 2
Concentrations (ng/g dry weight) of PAHs in the soil samples collected in Gwangju, Korea.

PAHs	Abbreviation	TEF[a]	School area				Residential area			
			Max	Min	Mean	Median	Max	Min	Mean	Median
Naphthalene	Nap	0.001	4.7	3.7	4.3	4.3	11.8	3.4	5.4	4.8
2-methyl naphthalene	2-MN		4.1	2.3	3.4	3.6	5.8	0.0	3.4	3.8
1-methyl naphthalene	1-MN		4.1	1.9	3.3	3.8	5.7	0.0	3.4	4.0
Acenaphthylene	Acl	0.001	ND	ND	–	–	0.4	ND	–	–
Acenaphthene	Ace	0.001	5.1	ND	2.7	1.9	7.1	ND	3.0	2.4
Fluorine	Flu	0.001	5.1	ND	3.5	4.5	6.7	ND	4.1	4.8
Phenanthrene	Phe	0.001	7.3	3.6	5.6	6.0	15.1	3.3	6.9	6.7
Anthracene	Ant	0.01	9.5	3.0	7.1	8.6	16.7	2.9	7.8	8.5
Fluoranthene	Flt	0.001	8.7	5.2	7.0	6.8	31.2	4.8	9.4	7.1
Pyrene	Pyr	0.001	8.6	5.8	7.0	6.9	25.9	5.4	9.4	7.2
Retene	Ret		9.3	6.9	7.8	7.8	11.4	ND	8.0	8.3
Benz[*a*]anthracene	BaA	0.1	6.9	5.8	6.2	6.1	13.9	6.2	7.9	6.9
Chrysene	Chr	0.01	11.4	8.9	9.6	9.5	17.3	9.0	11.0	10.3
Benzo[*k*]fluoranthene	BkF	0.01	14.4	6.5	9.7	9.0	18.3	7.7	11.3	9.8
Benzo[*b*]fluoranthene	BbF	0.1	12.9	9.3	10.6	10.6	16.4	9.5	11.8	11.4
Benzo[*e*]pyrene	BeP		9.3	7.8	8.5	8.4	12.7	8.1	9.6	9.0
Benzo[*a*]pyrene	BaP	1	9.8	8.6	9.3	9.4	17.7	8.8	10.6	9.6
Perlene	Per		10.7	8.3	9.2	9.0	12.2	8.5	9.9	9.4
Indeno[1,2,3-*cd*]pyrene	IcdP	0.1	18.9	ND	9.9	7.9	20.9	7.6	12.4	8.8
Dibenz[*a, h*]anthracene	DBahA	1	20.3	ND	2.9	–	10.4	ND	0.8	–
Benzo[*g,h,i*]pyrene	BghiP	0.01	11.1	8.2	9.3	8.8	16.8	8.4	11.1	10.7
Dibenzo[*a,l*]pyrene	DBalP		17.8	ND	4.6	–	8.2	ND	3.2	–
Dibenzo[*a,e*]pyrene + Coronene	DBaeP + Cor		12.9	7.7	9.3	8.1	14.9	7.7	10.7	9.4
	Σ_{23} PAHs		184	125	151	145	273	120	171	158
	$\Sigma_{16\text{-EPA}}$ PAHs		123	87	105	99	212	95	122	110
	ΣC– PAHs		82	41	58	60	101	49	66	62

ND: not detected.
Σ_{23} PAHs: sum of each analyte concentration.
$\Sigma_{16\text{-US EPA}}$ PAHs: Nap + Acl + Ace + Flu + Phe + Ant + Flt + Pyr + BaA + Chr + BkF + BbF + BaP + IcdP + DBahA + BghiP.
ΣC-PAHs: BaA + BbF + BkF + BaP + IcdP + DBahA.
[a] data cited in Nisbet and LaGoy (1992).

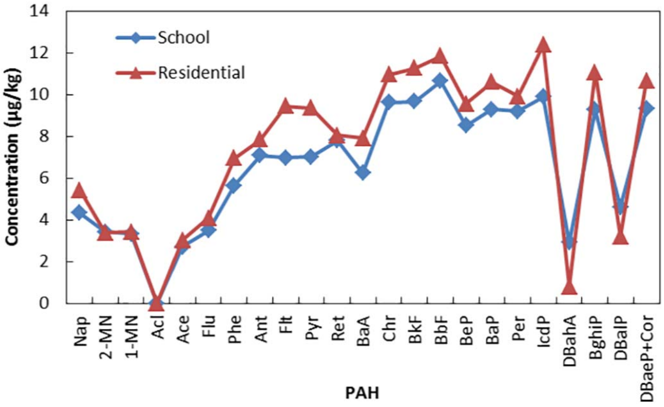

Fig. 2. Concentration of each PAH scattering diagram between school and residential areas.

2012; Yunker et al., 2002). A ratio of BaP/BghiP of < 0.6 indicates a non-traffic emission and that of > 0.6 is characteristic of a traffic source (Katsoyiannis et al., 2007).

2.3.2. *Principle component analysis (PCA)*

PCA, as a multivariate analytical tool, was applied for further investigations of possible sources of PAH contamination in soil samples. The principle component method with correlation matrix analysis was adopted in the extraction of main components for analysing relationships among the variables. Variables with similar characteristics (high loading value) were grouped into three factors called principle components (PCs) that defined as PC1, PC2 and PC3 based on the high percentage of variance and their eigenvalues (> 1). The results of PCA showed the primary portion of data variance through these factors; therefore, the PAHs representative of each PC were selected as source tracers. PCA analyses were performed using SPSS 11.0 software. Bartlett's test was used to determine the correlations between the variables and was considered statistically significant if p value was < 0.05.

2.4. *Soil toxicity assessment*

The assessment of soil toxicity in this study was performed based on IARC listed carcinogenic PAHs (ΣC-PAHs), including BaA, BbF, BkF, BaP, IcdP, and DBahA and BaP toxic equivalency factors (TEFs). Toxic equivalent quantities (TEQ$_s$) was calculated by multiplying the concentration of $\Sigma_{16\text{-EPA}}$ PAHs by the corresponding TEF value (given in Table 2), which was used to assess the potential health risk (Bortey-Sam et al., 2014; IARC, 1987; Jiang et al., 2009; Yang et al., 2013; Zhang et al., 2013).

The incremental lifetime cancer risk (ILCR) approach was employed to quantitatively estimate the exposure risk for $_{16\text{-EPA}}$ PAHs, exposed to soil through three main pathways. The ILCRs in terms of ingestion, dermal contact and inhalation were calculated based on the US EPA standard models (Chen and Liao, 2006; U.S.EPA, 1991), which are widely used by many authors to evaluate the ILCR value (Chen et al., 2013; Wang et al., 2011; Yu et al., 2014). Monte Carlo simulation was applied to evaluate the cancer risk using the software Crystal Ball 7.2 in order to minimize the uncertainties of the above calculations.

2.5. *Statistical analysis*

To determine the relationship between soil organic matter (SOM), moisture content and total PAHs for each sampling site, the linear correlation analyses were performed.

3. Results and discussion

3.1. *Concentration of PAHs*

The concentrations of twenty-three individual PAHs analyzed in urban soil (residential and school areas) as well as the sum of sixteen US EPA priority PAHs and ΣC-PAHs are presented in Table 2. The total concentrations of twenty-three PAHs (Σ_{23} PAHs) and sixteen PAHs ($\Sigma_{16\text{-EPA}}$ PAHs) varied in a narrow range, from 120 to 273 ng/g and from 95 to 212 ng/g, respectively, in residential areas, and from 125 to 184 ng/g and from 87 to 123 ng/g, respectively, in school areas. The variation of PAHs concentrations may be explained by the differences in traffic density and industrial emissions among the sites.

Regarding the sampling area, the mean concentrations of $\Sigma_{16\text{-EPA}}$ PAHs were 122 and 105 ng/g in the residential and school areas, respectively. The highest Σ_{23} PAHs concentrations were found at site R03 (residential area) (273 ng/g), following by site R01 (252 ng/g) compared with other present study sites. This might be attributed to vehicular emissions and coal combustion since these sites were located 1.5–2 km from the Hanam (R03) and Pyeongdong (R01) industrial area. Thus, these sites might be substantially polluted by the PAHs emitted from both the industrial facilities and many heavy vehicles passing by these sites. In this study, the soil samples from residential areas had higher concentrations of PAHs than those in the school areas, probably due to the domestic heating and cooking facilities in the residential areas. Therefore, the soil samples from residential areas might together be affected by the PAHs emitted from vehicular emissions, as well as industrial and residential activities. In contrast, the average concentration of each individual PAH for the school and residential areas reflected the similarity between two areas (Fig. 2), which indicating that the PAHs may be from the similar emission sources. Overall, the concentrations of Σ_{23} PAHs in soil from twenty sampling sites ranging from 120 to 273 ng/g with an average value of 164 ng/g were compared with those of previous studies conducted in Asian countries (Table 3). The levels of PAHs in this study were significantly lower than those in the urban soils of Shanghai, China (Jiang et al., 2009), Delhi, India (Agarwal et al., 2009), Beijing, China (Li et al., 2006), and Ulsan, Korea (Kwon and Choi, 2014). In comparison to other areas around the world, the average total PAH concentration was found lower than those in the surface soils from the Kumasi, Ghana (442.5 ng/g) (Bortey-Sam et al., 2014) and Birmingham, UK (Smith et al., 1995).

Table 3
Concentration (ng/g, dry weight) of ΣPAHs in soils from other areas of the world.

Sample	Number of PAHs	Mean concentrations of PAHs			Reference
		Σ_{all} PAHs	$\Sigma_{16\text{-US EPA}}$ PAHs	ΣC-PAHs	
Mixed soil samples of the Ulsan city, South Korea	16	960	960	430	Kwon and Choi (2014)
Urban soils of the megacity Shanghai	26	2420	1970	–	Wang et al. (2013)
Surface soils of the Yellow River Delta, China	16	118	118	–	Yuan et al. (2014)
Urban soil from Beijing, China	16	1640	1640	–	Li et al. (2006)
Residential soil from Agra, India	16	937	937	–	Masih and Taneja (2006)
Soil samples from Delhi, India	16	1910	1910	–	Agarwal et al. (2009)
Surface soil of Gwangju city, South Korea	23	164	116	63	This study

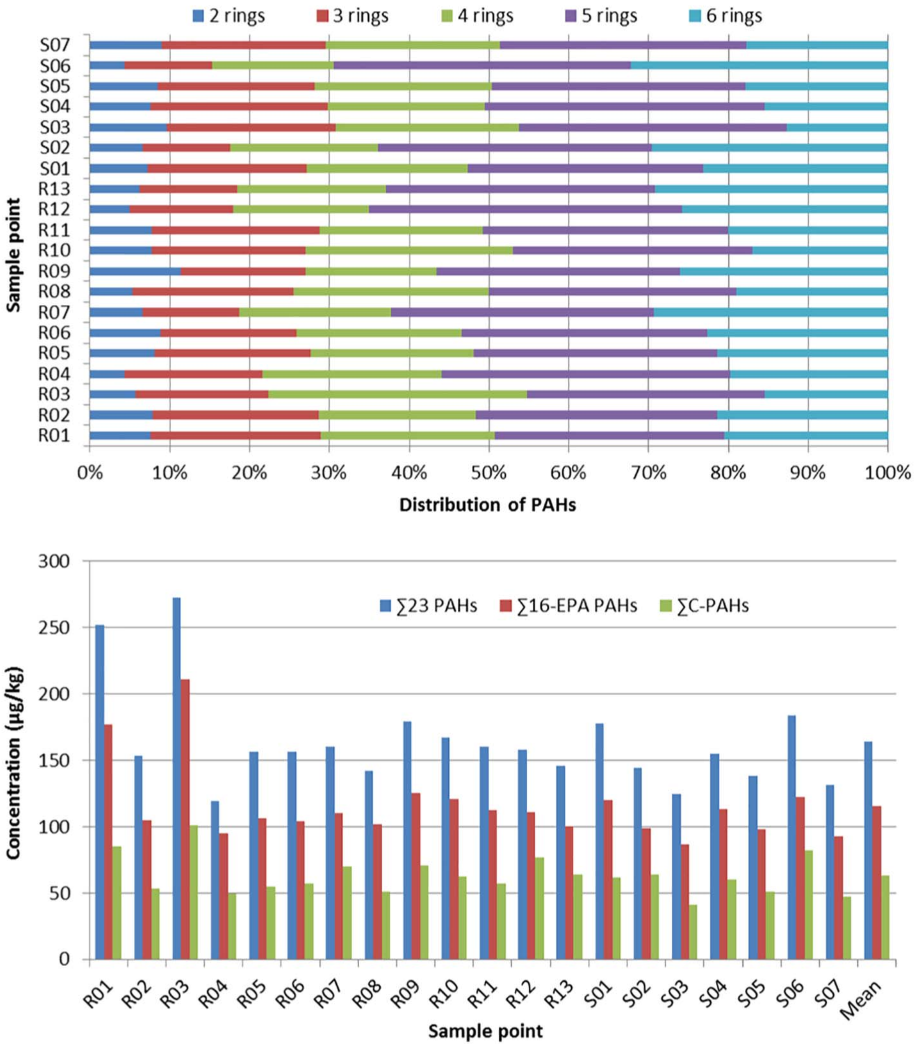

Fig. 3. Concentration and composition profile of PAHs at each sampling site.

3.2. Correlation between PAHs and SOM/moisture content

The moisture content and SOM varied greatly among the soil samples. The moisture content of soils ranged from 0.28% to 30.55%, with a mean value of 6.86% and the SOM ranged from 1.64% to 15.24% with a mean value of 4.97%. The correlations had tested between the concentration of PAHs vs. SOM and PAHs vs. moisture content. Several studies suggested that some factors such as SOM and temperature could affect the yield and distribution of PAHs, while soil with high organic matter was considered to be the important reservoir for the PAHs in the environment (Baumard et al., 1999; Pozo et al., 2011). No significant correlations were found between the concentration of PAHs and SOM ($r^2 = 0.06$) in this study. This is because the soil samples collected have high contents of sand particles which lead to less PAHs adsorption by soils. Another possible reason for the lack of correlation between SOM and PAHs is that the concentration of PAHs might be affected by the distances between the point and/or non-point pollution sources and the weather parameters such as temperature and wind speed or direction. Similar correlation was observed for the concentration of PAHs and moisture content in soil samples ($r^2 = 0.07$), therefore, soil moisture does not appear to influence the PAHs distribution in the area.

3.3. Molecular distribution of PAHs

The concentration of ΣC-PAHs ranged from 41 to 102 ng/g with a mean value of 63 ng/g, which was relatively lower than that for Ulsan, Korea (430 ng/g) (Kwon and Choi, 2014). ΣC-PAHs accounted for about 38% of total PAHs in soil samples. The PAHs were separated into five groups according to the number of aromatic rings. The percentage contribution of each group and the contribution level (ng/g) of $\Sigma_{16\text{-EPA}}$ PAHs and ΣC-PAHs to total PAHs at each sampling site were depicted in Fig. 3. High molecular weight PAHs (5- and − 6 ring) were predominant in the soil samples, followed by 4-ring PAHs, while the fraction of 2-ring PAHs was the lowest. Similar findings were reported by other authors, where PAHs were dominated by high molecular weight compounds (4–6 rings) (Nguyen et al., 2014; Wang et al., 2009). The molecular distribution of PAHs from the sampling sites was similar, which also suggests that emission sources in these areas were similar, with the exception of the sites R07, R12, R13, S02, and S06. At site S06, the fraction of PAHs (5- and 6-ring) was found to be the highest (70%). The high concentrations of 5- and 6-ring PAHs could result from vehicular emission since site S06 was located in the school campus in the downtown area, which is 2.5 km from the bus terminal and 2.8 km from the motor plant.

3.4. Source identification based on the composition of PAHs

Based on several indexes, the origin of PAHs was determined in the soil samples, and the results are presented in Table 4. Considering the ratio of BaP/BghiP, the values ranged from 0.88 to 1.15 in soil samples, indicating a PAH contribution mainly from traffic emission for all sampling sites, according to the literature (Katsoyiannis et al., 2007). The ratio of IcdP/(IcdP + BghiP) for six samples was greater 0.5, probably because the incineration plant was located near these

Table 4
Diagnostic ratios of PAHs.

Sampling site	BaP/BghiP[a]	Flt/(Flt + Pyr)[b]	BaA/(BaA + Chr)[c]	Ant/(Ant + Phe)[d]	Flu/(Flu + Pyr)[e]
R01	0.76	0.51	0.38	0.59	0.31
R02	1.03	0.50	0.40	0.58	0.41
R03	1.28	0.55	0.45	0.36	0.19
R04	1.05	0.49	0.41	0.56	0.43
R05	1.05	0.50	0.41	0.44	0.40
R06	0.95	0.48	0.45	0.57	0.41
R07	0.87	0.47	0.43	0.46	0.38
R08	0.91	0.46	0.37	0.56	0.33
R09	0.88	0.46	0.40	0.57	0.04
R10	0.86	0.51	0.49	0.57	0.31
R11	0.95	0.50	0.41	0.57	0.37
R12	1.05	0.47	0.44	0.46	0.26
R13	0.88	0.47	0.41	0.57	–
S01	1.05	0.50	0.38	0.57	0.37
S02	0.88	0.47	0.39	0.45	–
S03	1.06	0.49	0.44	0.47	0.40
S04	1.15	0.50	0.38	0.58	0.38
S05	1.00	0.52	0.39	0.60	0.38
S06	0.88	0.49	0.38	0.57	0.16
S07	1.06	0.50	0.40	0.58	0.40

[a] < 0.6 non-traffic emission; > 0.6 traffic emission (Katsoyiannis et al., 2007).

[b] < 0.4 petroleum; 0.4–0.5 fossil fuel combustion; > 0.5 coal and biomass combustion (De La Torre-Roche et al., 2009).

[c] < 0.2 petroleum; 0.2–0.35 coal combustion; > 0.35 vehicular emission (Akyüz and Çabuk, 2010).

[d] < 0.1 petroleum; > 0.1 pyrogenic (Yunker et al., 2002).

[e] < 0.5 petrol emission; > 0.5 diesel emission (Ravindra et al., 2008).

sampling sites. This indicates that the input of PAHs was derived from coal or biomass combustion. The cross plot between Flt/(Flt + Pyr) and IcdP/(IcdP + BghiP) represents the mixed source of PAHs (Fig. 4). For Ant/(Ant + Phe), the ratios at all sites were higher than 0.1, indicating that the main PAH source was from fuel and coal combustion sources (Yunker et al., 2002). The BaA/(BaA + Chr) ratios for all soil samples were above 0.35, indicating the vehicular emission contribution of PAHs (Akyüz and Çabuk, 2010). Considering all five diagnostic ratios, it is found that the pollution sources of PAHs in the soil were derived mainly from vehicular emissions and fossil fuel combustion.

3.5. *Source apportionment using PCA*

As shown in Table 2, among all PAHs, IcdP, BbF, BkF, Chr, BghiP, and BaP were the most dominant species, which was in accordance with the results deduced from the PCA. Based on the component extract from the PCA, it was revealed that three factors were responsible for PAHs in the surface soil of Gwangju City, and accounted for 73.7% of the total variance (Table 5). Among them, PC1 explained 38.8% of the total variance and was highly loaded with Phe, Flt, Pyr, BaA, Chr, BkF, BbF, BeP, and BaP. About 22% of variance was explained by PC2, which was characterized by high loading of Per, IndP, BghiP, and DBaeP + Cor. The last factor was PC3 (12.9% of variance), which had high loading values of Nap, 2- and 1-MN, Acl, and Ant.

The schematic view of source apportionment by PCA is shown in Fig. 5. As it can be seen that, PC1 accounts for the maximum variability and had a high loading with Pyr, BaA, Chr, BkF, BbF, BeP, and BaP, which are the chemical signs of fuel and coal combustion sources (Fang et al., 2004; Guo et al., 2003; Harrison et al., 1996; Khalili et al., 1995). BaA and BbF are often resulted from the combustion of fossil fuel, as reported by Rogge et al. (1993). Pyr and BaP are markers of for coal combustion (Simcik et al., 1999; Yuan et al., 2014). Per, IndP and BghiP predominated from the gasoline engine emission (Khalili et al., 1995; Larsen and Baker, 2003). Overall, PC1 and PC2 are related to coal and fossil fuel (regardless of the fuel types) combustion, indicating the mixed pyrogenic sources. PC3 included four PAHs. The components of PC3 consist of 2–3 ring PAHs and may have originated from oil and low temperature or incomplete combustion (Dong and Lee, 2009; Wang et al., 2009). Therefore, the factor PC3 appears to be associated with biomass and/or incomplete combustion. In summary, the mixed pyrogenic can be assumed to be the major sources of PAHs in the soil of Gwangju City.

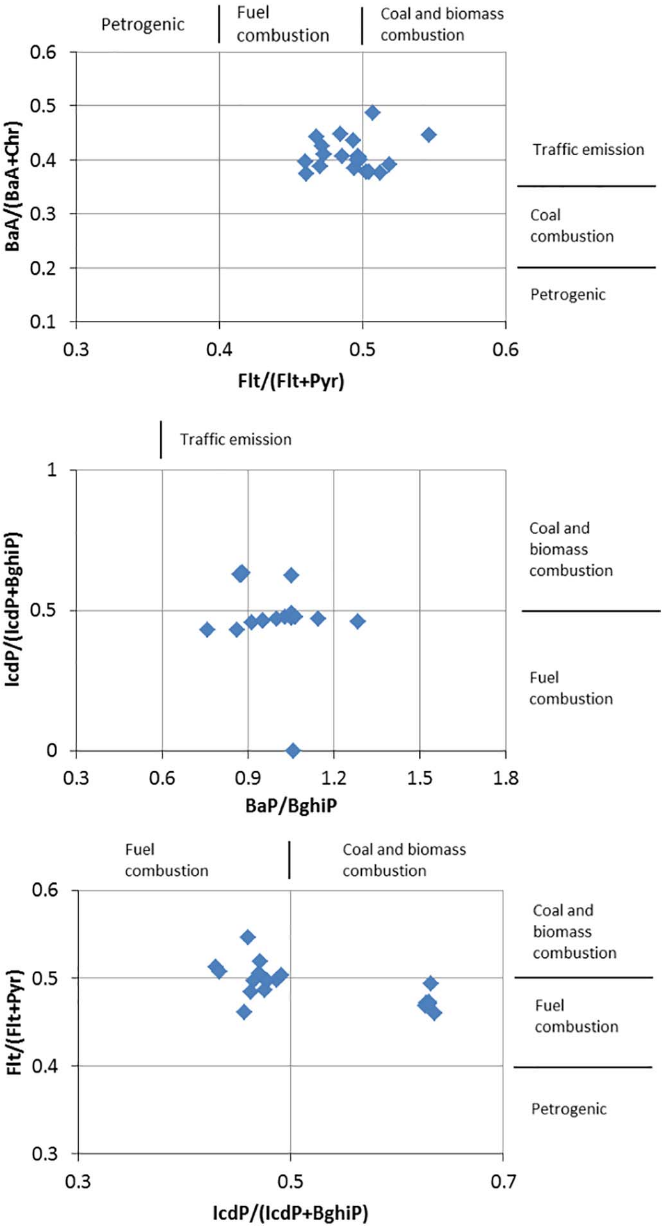

Fig. 4. Cross plot for the isomeric ratios.

PCA was also undertaken for each sampling site to examine the differences in source type and these results are presented in Table 6. The PCA results indicated that the soil samples could be divided into two main groups (80% of the variance explained) and were characterized by mixed pyrogenic and petrogenic sources including fossil fuel combustion and vehicular emission (diesel and gasoline). Similar results were also reported for other cities in Korea (Dong and Lee, 2009; Kwon and Choi, 2014). Dong and Lee (2009) reported that PAHs in road dust from Ulsan originate from four main sources: diesel vehicular emissions, oil combustion, gasoline vehicular emissions, and coal combustion.

Moreover, in order to perform a further study of the source identification of PAHs, the correlation between individual samples for each

Table 5
Factor analysis scores following Varimax rotation for each PAH.

PAH	Component		
	PC-1	PC-2	PC-3
Nap	0.128	0.471	0.679
2-MN	0.45	0.132	0.653
1-MN	0.545	− 0.327	0.63
Acl	− 0.225	0.46	0.595
Ace	0.502	− 0.116	0.12
Flu	0.597	− 0.66	0.158
Phe	0.911	− 0.12	0.288
Ant	0.516	− 0.226	0.586
Flt	0.946	− 0.016	− 0.024
Pyr	0.949	0.002	0.007
Ret	0.436	0.248	0.457
BaA	0.846	0.116	0.04
Chr	0.947	0.193	0.156
BkF	0.627	0.298	0.237
BbF	0.776	0.396	0.268
BeP	0.713	0.618	0.211
BaP	0.864	0.371	− 0.023
Per	0.349	0.898	0.117
IcdP	− 0.102	0.954	− 0.104
DBahA	0.339	0.25	− 0.572
BghiP	0.636	0.664	0.207
DBalP	0.365	− 0.026	− 0.232
DBaeP + Cor	0.099	0.956	0.086
% of variance	38.8	22	12.9

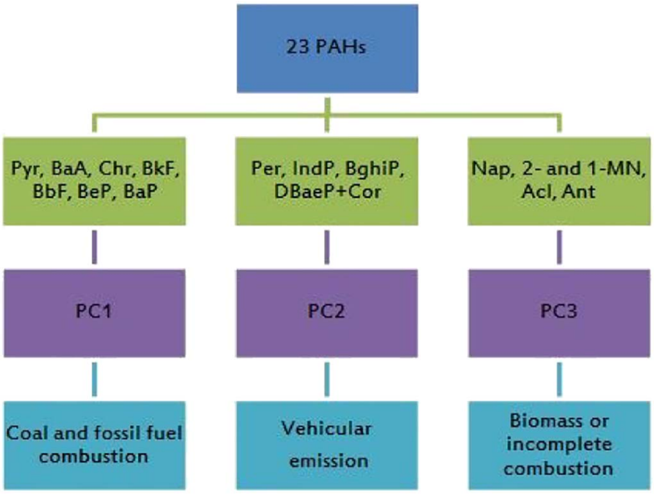

Fig. 5. The schematic view of source apportionment by PCA.

analyte was determined. A high correlation was observed (correlation coefficient > 0.90, $p < 0.01$) between the analyte content in the R01, R02, R03, R06, R10, R11, and S03 samples; while the samples collected at R07, R09, R12, R13, and S02 had a high correlation (correlation coefficient > 0.90, $p < 0.01$). This observation was consistent with the PCA results of source identification for individual samples.

3.6. Soil potential toxicity and health risk assessment

Among the PAHs, the total concentrations of ΣC-PAHs are of high concern due to their potentially carcinogenic toxicity (IARC, 1987; Yuan et al., 2014). BaP is the highest carcinogenic contributor (Bortey-Sam et al., 2014; Halek et al., 2008). The concentration of ΣC-PAHs ranged from 41 to 102 ng/g with a mean concentration of 63 ng/g, which is relatively higher than the values in the previous study conducted in Niger Delta, South Nigeria (4.7–10.2 ng/g) (Olajire et al., 2005), but much lower than those in Kumasi, Ghana (321–1072 ng/g) (Bortey-Sam et al., 2014), while similar values were found in the wetland soil of Liaohe estuary with a mean value of 82.6 ng/g (Li et al., 2014). ΣC-PAHs accounted for 54% of $\Sigma_{16\text{-EPA}}$ PAHs. This value was higher than that in Kumasi, Ghana (43%) and in Liaohe (38%).

The total TEQs of $_{16\text{-EPA}}$ PAHs in soil samples ranged from 11.26 to 34.25 ng/g, with an average value of 14.3 ng/g. Higher TEQ values were obtained at sites S06, R01, R07, and R12 due to the presence of greater concentrations of high molecular weight PAHs (5–6 rings) (Fig. 3) which are more toxic than the low molecular weight PAHs. It was worth noting that TEQ of carcinogenic PAHs were the main contributors to the total TEQ of the soil samples, accounting for about 98%. For individual PAHs, TEQ had the following order: BaP (63%) > DBahA (10%) > IcdP (7%) > BaA (5%).

Table 6
Factor analysis scores following Varimax rotation for each sampling site.

Sampling site	Component		
	PC-1	PC-2	PC-3
R01	0.868	0.391	0.138
R02	0.833	0.354	0.359
R03	0.647	0.566	0.016
R04	0.683	0.084	0.083
R05	0.777	0.483	0.261
R06	0.758	0.468	0.31
R07	0.335	0.906	0.19
R08	0.772	0.55	− 0.034
R09	0.321	0.894	0.123
R10	0.824	0.475	− 0.095
R11	0.856	0.455	0.177
R12	0.422	0.81	0.222
R13	0.354	0.902	0.219
S011	0.763	0.129	0.575
S02	0.33	0.906	0.225
S03	0.813	0.276	− 0.279
S04	0.789	0.499	− 0.056
S05	0.77	0.59	− 0.074
S06	− 0.059	0.313	0.847
S07	0.747	0.595	− 0.102
% of variance	45.8	34.2	8.5

Table 7
Risk variables considered in the ILCR assessment. Table adopted from Chen et al. (2013).

Exposure variable	Abbreviation	Unit	Child	Adult
Body weight	BW	kg	18.6	71.6
Exposure frequency	EF	day/year	250	250
Exposure duration	ED	year	6	24
Dust ingestion rate	IR_{soil}	mg/day	174	100
Inhalation rate	IR_{air}	m^3/day	9.3	16.3
Dermal exposure area	SA	cm^2	2000	5800
Dermal adherence factor	AF	mg/cm^2	0.25	1
Dermal adsorption fraction	ABS	–	0.13	0.13
Average life span	AT	day	70 × 365	70 × 365
Particle emission factor	PEF	m^3/kg	1.36×10^9	1.36×10^9
	$CSF_{Ingestion}$	$(mg/kg/d)^{-1}$	7.3	
	CSF_{Dermal}	$(mg/kg/d)^{-1}$	25	
	$CSF_{Inhalation}$	$(mg/kg/d)^{-1}$	3.85	

Table 8
Risk of cancer due to human exposure to soil PAHs.

Exposure pathways	Child	Adult
Ingestion	8.30E-06	7.72E-06
Dermal	3.10E-06	5.83E-05
Inhalation	5.04E-11	1.44E-10

Parameters referred to in the ILCR models for children and adults were based on the risk assessment guidance and related publications shown in Table 7. The 95th percentiles cancer risks for children and adults regardless of sampling point, indicating a low human health risk from the exposure of direct ingestion and inhalation (Table 8). The dermal contact appeared to be the predominant exposure pathway for adults that induced a potential risk (with 95th percentiles of 5.83×10^{-6}) when compared to children. This result may be cause that the dermal surface exposure and exposure duration of adults were higher than those of children. This findings was similar to the human cancer risk resulted from PAHs exposure in urban dust of Guangzhou, China (Wang et al., 2011). In general, an ILCR between 10^{-6} and 10^{-4} indicate potential risk where a potential high risk denotes with an ILCR of $> 10^{-4}$ (Chen and Liao, 2006). In this study, the cancer risks for two age groups were below 10^{-4}, there is no potential high cancer risk due to exposed to PAHs in surface soils of Gwangju, Korea.

4. Conclusions

This study provided information on the priority hazard PAH occurrence in surface soil in Gwangju, Korea with the levels and possible emission sources. The concentrations of total PAHs and $\Sigma_{16\text{-EPA}}$ PAHs ranged from 120 to 273 ng/g and 87 to 212 ng/g, respectively, with a mean value of 164 and 116 ng/g, respectively. The level of PAH concentrations in this study area were low in comparison with other cities in Asian countries. The results of the molecular fraction of PAHs showed that the contents of analytes in soil samples were dominated by higher molecular weight compounds (4–6 ring), accounting for 70–80% of the total PAHs. The different diagnostic ratios and PCA demonstrated that the origin of PAHs in the samples is connected with mixed pyrogenic sources (coal and fossil fuel combustion), contributing to 74% of the total PAHs. BaP was the main contributor to TEQ (63%), although the level of toxicity does not appear to be significant in comparison with other cities. The ILCRs of PAHs showed that the cancer risks for two age groups were at acceptable range, there is no potential high cancer risk.

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