



Assessment of carcinogenic risk due to inhalation of polycyclic aromatic hydrocarbons in PM₁₀ from an industrial city: A Korean case-study

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ABSTRACT

This study investigated the effects of meteorological conditions and spatial variations on the toxicity of polycyclic aromatic hydrocarbons (PAHs) in airborne PM₁₀ in Ulsan, the largest industrial city in Korea. Daily PM₁₀ samples were collected on quartz microfiber filters using high volume samplers located in a downtown area, a residential area and an industrial area of Ulsan during spring and summer sampling periods. Sixteen individual PAHs were extracted into a mixture solution of dichloromethane and n-hexane (1:1, v/v) in an ultrasonic bath and were analyzed using a high performance liquid chromatography system with an ultra-violet detector (HPLC-UVD). The average total PAH concentrations from the three representative sampling sites of Ulsan ranged from 16.15 to 57.12 ng/m³ in spring and from 11.11 to 34.56 ng/m³ in summer. The toxicity equivalent concentrations (TEQs) of the PAHs in PM₁₀ of Ulsan ranged from 1.82 to 13.1 ng/m³, with an average level of 4.17 ng/m³. The highest TEQs were found in the downtown area, which had an average value of 6.30 ng/m³ in spring and 5.52 ng/m³ in summer. BaP and DahA were identified as the major carcinogenic PAHs that contributed to 34.8 and 59.4% of the total carcinogenic potency of PAHs in PM₁₀ in Ulsan. The identified TEQs were highly correlated ($r^2 = 0.73$ – 0.90 , $p < 0.01$) with the total PAH concentrations for each area. The TEQs showed a significant correlation ($p < 0.01$) with the concentration of air pollutants, including PM₁₀, PM_{2.5} and NO₂.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) consist of several hundred individual organic compounds which contain two or more fused aromatic rings [1,2]. PAHs are classified as one of the most hazardous air pollutants, causing serious health problems including skin/eye irritation and immunogenic-toxicity [1–3]. The most serious health problem associated with PAHs is carcinogenicity [3]. For example, some PAHs such as benzo[a]pyrene (BaP) and dibenzo[a,h]anthracene (DahA) have been reported as carcinogenic organic compounds [2–4]. Once PAHs are released into the atmosphere, they are predominantly associated with particulate matter (PM) such as PM₁₀. In addition, PM₁₀ is well-known to affect human thoracic health. The occurrence of PAHs in PM₁₀ which linked to the adverse health problems, especially lung cancer, was observed in some epidemiological studies [5,6]. Thus, atmospheric pollution of PAHs contained in PM₁₀ is recently a serious environment issue of major concern.

Incomplete combustion and pyrolysis of organic fuels are major sources of airborne PAHs [7,8]. Due to their widespread sources and persistent characteristics, PAHs are dispersed through atmospheric

transport and exist almost everywhere. Human beings are exposed to vapor or particulate phases of PAHs in ambient air or indoor environments such as homes or workplaces. Pathways of human exposure to PAHs include air emissions from cigarette smoke, vehicle exhaust, residential heating, agricultural burning and industrial processes. According to the United States Agency for Toxic Substances and Disease Registry (ATSDR), main exposures of the U.S. population to PAHs include the inhalation of tobacco smoke, wood smoke, ambient air contamination with PAHs from traffic emissions and consumption of food containing PAHs such as meat or milk. Vehicle emissions are the main sources of PAHs in ambient air around urban areas [9].

Some of PAHs are classified as carcinogenic materials by the United State Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC) [2–4]. Based on the epidemiological studies of inhalatory PAH uptake, the health risk of PAHs was evaluated [10]. Three approaches exist for the carcinogenic risk assessment of PAHs: toxic equivalency factors (TEFs), the comparative potency of mixtures and the use of BaP as a surrogate [1,10]. Pufulete et al. reported that the TEFs method is preferable over the other two methods for the determination of inhalation carcinogenic potencies of relevant PAHs in ambient air [10]. Petry et al. used the TEFs method to estimate occupational and environmental health risks associated with exposure to airborne mixtures of PAHs [11]. The present study utilized toxic equivalent

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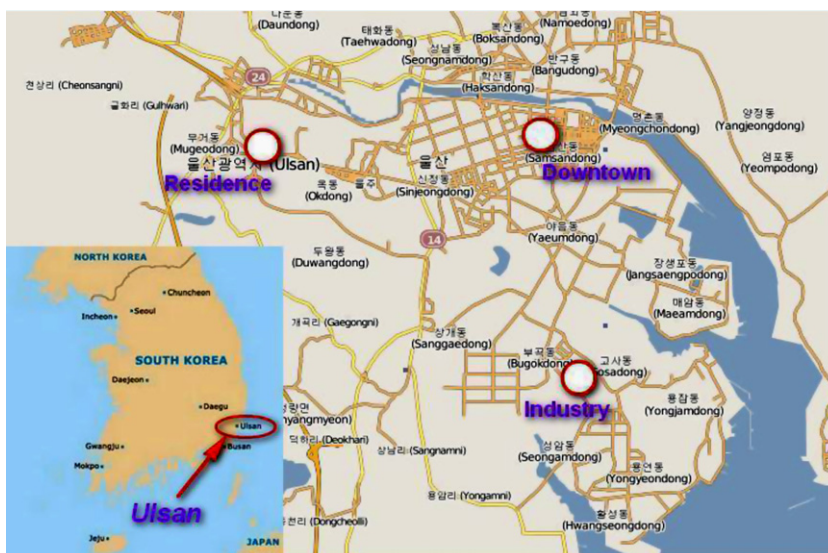


Fig. 1. Airborne PM₁₀ sampling sites in Ulsan.

factors (TEFs) systems to estimate the inhalation risks of individual and total PAHs to human health. This study also identified the influences of seasonal and spatial variations on the toxicity of PAHs contained in PM₁₀ and the relationships of PAH toxicity with air pollutants, including SO₂, NO₂, O₃, PM and CO.

2. Materials and methods

2.1. Sampling sites

Ulsan is the largest industrial city in Korea, with a population of more than 1.1 million, and it has coastal regions in the southern and eastern sites. Three sampling areas which include downtown (DT), residential (RS) and industrial complex (IC) areas were selected to measure the ambient air PAH concentrations in Ulsan (Fig. 1).

In the downtown and residential areas, airborne PM₁₀ samples were collected from the roofs of district offices surrounded by nearby traffic roads. The average traffic intensities of the roads were 26,289 and 21,263 vehicles per day in the residential and downtown areas, respectively. The eight-lane Ulsan highways are located 150 m far from the residential area, and the downtown area is located downwind side of petrochemical, automotive, manufacturing and shipbuilding complexes.

In the industrial complex area (IC), airborne PM₁₀ samples were obtained 500 m far from the central area of the petrochemical complexes. The main emission sources of existing air pollutants in the industrial complex are mainly associated with the production of chemicals and petrochemicals, waste incineration and transportation of industrial products.

2.2. Sample collection

Daily PM₁₀ samples were collected from the three sampling sites using a high volume air sampler (Tisch Environ, Inc.) from May to September 2009. A total of 21 late spring samples were obtained from May to early June, and a total of 21 summer samples were obtained between July and early September. Due to the monsoon season and its heavy rains during the summer sampling period, a longer sampling period was required. The meteorological conditions in each sampling site during the sampling periods were summarized in Table 1. The flow rate of the Tisch sampler was 1.13 m³/min, and PM₁₀ samples were collected on quartz

microfiber filters (QMA, 20.3 cm × 25.4 cm, Whatman), which were heated in an oven at 450 °C for 6 h in order to volatilize the organic matter content prior to use. Collected PM₁₀ samples were stored in a refrigerator at temperatures of below 4 °C until extraction and analysis.

2.3. Sample extraction and analysis

The sample filters were cut into small pieces (0.5 mm × 2 mm) and were extracted three times with 120 ml of a mixture of n-hexane and dichloromethane (1:1, v/v) in an ultrasonic bath (Sibata, BIP-1200) at room temperature; the extract was filtered and concentrated to 1 ml at 30 °C by a nitrogen concentrator. An extract of 20 μl was injected into a high performance liquid chromatograph equipped with a UV detector (HPLC-UV) and a 4.6 mm (ID) × 150 mm (L) C18 steel column (Varian, USA) and was detected at 254 nm. A mixture of methanol (MeOH) and water was used for the mobile phase, which was pumped at a flow rate of 1.0 ml/min at 35 °C. The 16 priority PAHs suggested by the US Environmental Protection Agency (US EPA) were analyzed. The analysis results included naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), flourene (Flu), phenanthrene (PA), anthracene (Ant), flouranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]flouranthene (BbF), benzo[k]flouranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP), and indeno[1,2,3-cd]pyrene (Ind).

2.4. Quality control

Fields blanks were used to determine background contamination, and the 16 selected PAH concentrations in the blank samples were below the detection limits. The recovery rates and relative standard deviations (RSD %) of each measured PAH are presented in Table 2. The ambient air concentrations of PAHs in the collected PM₁₀ samples were corrected based on the recovery efficiency of each PAH.

The hourly concentrations of airborne pollutants and meteorological data were measured by the air monitoring sites at/near three sampling areas during the sampling periods. The average concentrations and standard deviations of airborne pollutants were calculated using an SPSS package (version 16.0).

Table 1
The meteorological conditions during the sampling periods in Ulsan.

	Sampling periods						
	Late spring	May–June 2009			Summer	July–September 2009	
	DT ^a	RS ^a	IC ^a	DT ^a	RS ^a	IC ^a	
Temp (°C)	19.1 ± 1.8	21.3 ± 2.0	23.6 ± 2.2	25.7 ± 1.9	24.5 ± 2.2	24.9 ± 2.1	
WS (m/s)	3.2 ± 1.4	2.4 ± 0.6	1.9 ± 0.4	2.3 ± 0.6	2.2 ± 0.7	2.2 ± 0.4	
Wind directions	NE, N	E, SSW	S, SSE	EN, WWS	SSW	NE, N	
RH (%)	70.4 ± 27.3	69.6 ± 10.6	67.8 ± 18.2	74.2 ± 4.6	75.2 ± 3.2	78.0 ± 1.5	
Rainfall (mm)	321.0	321.0	321.0	493.7	493.7	493.7	
SD (h)	7.9 ± 5.3	6.8 ± 4.4	8.2 ± 4.2	8.1 ± 3.0	7.2 ± 2.8	7.0 ± 3.4	

DT, downtown; RS, residential area; IC, industrial complex. Temp, temperature (°C); WS, wind speed (m/s); RH, relative humidity (%); SD, sunlight duration (h).

^a Areas.

Table 2
Molecular weight, number of rings, carcinogenicity classification, recovery rates and relative standard deviations of 16 PAHs.

PAH	Molecular weight	No. of ring	Carcinogenicity classification	Recovery (%)	RSD (%)
Nap	128	2	2B ^a	56.8	31.21
AcPy	154	3		55.5	1.42
AcP	152	3		62.9	4.14
Flu	178	3		67.3	9.01
PA	178	3		58.7	19.28
Ant	178	3		64.7	28.36
FL	202	4		92.9	3.78
Pyr	202	4		93.6	7.79
BaA	228	4	B2	110.3	10.65
Chry	228	4	B2	103.1	21.82
BbF	276	5	B2	89.9	16.04
BkF	252	5	B2	98.0	13.82
BaP	252	5	B2	99.3	7.89
DahA	278	5	B2	102.4	2.76
BghiP	276	6		117.4	9.43
Ind	276	6	B2	107.2	17.38

B2, a group of PAHs which are probably carcinogenic to human (US EPA, 1992).

^a Nap listed in 2B group (IARC [21]) which are possibly carcinogenic to human.

2.5. Toxicity evaluation method

The toxicities of PAHs in PM₁₀ were evaluated using the relative toxicity value of each individual PAH compound. The PAH toxicities of the PM₁₀ samples were calculated based on the set of toxic equivalency factors (TEFs) of PAHs proposed by Muller and Nisbest and LaGoy [12,13] (shown in Table 3). The TEFs system reported by Muller is the newest system for carcinogenic assessment due to inhalation of PAHs (cited by WHO [1]). However, the toxicities for Nap, AcPy, AcP, Flu and FL were not included in this system, thus those missing TEFs values of PAHs were adopted from the system of Nisbest and LaGoy, proposed in order to complete the determination of toxicity due to the inhalation of PAHs.

BaP is considered the most carcinogenic PAH and is often used as an indicator of human exposure to PAHs [14]. In the previous studies, BaP was assigned a TEFd system value of 1, and the toxicities of other PAHs were converted into TEFs relative to BaP [11,14–17]. The toxicity equivalency concentrations (TEQs) were calculated as the product of summation of the TEFs values and the concentration of each individual PAH. The equation, then, can be written as the following:

$$\text{TEQs} = \sum (C_i \times \text{TEF}_i)$$

where TEQs are the toxic equivalent concentrations of the identified PAHs and C_i and TEF_i are the concentration and toxic equivalency factor of PAH_{*i*}, respectively [18].

3. Results and discussion

3.1. Individual PAH concentrations in PM₁₀

Table 4 shows the average concentrations of PM₁₀, PM_{2.5} and other air pollutants including SO₂, NO₂, CO, and O₃ from the three sampling sites during the study periods.

Fig. 2 represents the seasonal average concentrations of the individual PAHs identified in airborne PM₁₀ from the three sampling sites during the spring and summer study periods. The determined average concentrations of the total PAHs from the three sampling sites, including a residential, downtown and industrial area in Ulsan, were 30.10 ± 10.49 ng/m³ in late spring and 21.93 ± 6.64 ng/m³ in summer. The average concentration of total PAHs in the late spring was almost 1.4 times higher than the average concentration of the summer. The common and dominant PAHs for both seasons at the three sites were Flu, PA, FL, Pyr and DahA, which may have originated from oil combustion or incineration [7,19,20]. Each site also showed different seasonal distribution patterns of PAHs. For example, the downtown area showed particularly high concentrations of DahA and Flu in both seasons compared to those of the residential and industrial sites. The industrial site showed particularly high spring concentrations of Flu, AcP and AcPy and high summer concentrations of Pyr and FL compared to those of the other sites. Based on a principal component analysis, the main source of PAHs was diesel emissions in the residential area and oil combustion in the industrial area.

According to the carcinogenic classification of PAHs by the US EPA, seven PAHs including BaA, BaP, BbF, BkF, Chry, DahA and Ind,

Table 3
Proposed TEFs for individual PAHs.

Compound	US EPA (1984)	Nisbet and LaGoy [13]	OEHHA [29]	Muller [12]	This study
Nap	0	0.001			0.001 ^a
AcPy	0	0.001			0.001 ^a
AcP	0	0.001			0.001 ^a
Flu	0	0.001			0.001 ^a
PA	0	0.001		0.00064	0.00064 ^b
Ant	0	0.01		0.28	0.28 ^b
FL	0	0.001			0.001 ^a
Pyr	0	0.001		0.001	0.001 ^{a,b}
BaA	1	0.1	0.1	0.014	0.014 ^b
Chry	1	0.01	0.01	0.026	0.026 ^b
BbF	1	0.1	0.1	0.11	0.11 ^b
BkF	1	0.1	0.1	0.037	0.037 ^b
BaP	1	1	1	1	1 ^{a,b}
DahA	1	1	0.4	0.89	0.89 ^b
BghiP	0	0.01		0.012	0.012 ^b
Ind	1	1	0.1	0.067	0.067 ^b

^a The TEF values proposed by Nisbest and Lagoy [13].

^b The TEF values proposed by Muller [12].

Table 4
The air pollutants concentrations and during the sampling periods in Ulsan.

	Sampling periods					
	Late spring			Summer		
	May–June 2009			July–September 2009		
	DT ^a	RS ^a	IC ^a	DT ^a	RS ^a	IC ^a
PM ₁₀	79.4 ± 32.5	35.07 ± 8.5	54.8 ± 7.8	47.5 ± 18.2	33.2 ± 12.6	39.3 ± 11.0
PM _{2.5}	42.9 ± 19.5	24.9 ± 7.0	32.1 ± 17.6	23.3 ± 8.0	15.9 ± 6.8	15.4 ± 7.2
SO ₂	0.009 ± 0.011	0.005 ± 0.006	0.013 ± 0.011	0.004 ± 0.003	0.004 ± 0.003	0.009 ± 0.008
NO ₂	0.028 ± 0.020	0.024 ± 0.013	0.027 ± 0.014	0.018 ± 0.011	0.021 ± 0.010	0.021 ± 0.010
O ₃	0.035 ± 0.021	0.032 ± 0.024	0.036 ± 0.018	0.025 ± 0.015	0.018 ± 0.017	0.027 ± 0.015
CO	0.351 ± 0.226	0.363 ± 0.156	0.468 ± 0.351	0.382 ± 0.169	0.329 ± 0.153	0.338 ± 0.216

DT, downtown area; RS, residential area; IC, industrial complex area. Unit: PM₁₀, PM_{2.5} (μg/m³); SO₂, NO₂, O₃, CO (ppm).

^a Areas.

as shown in Table 2, were classified as B2 groups, which were classified as probable carcinogenic compounds [2]. Naphthalene was listed as a chemical which was recognized to cause cancer by the State of California on April, 2002 and was classified as group 2B (possibly carcinogenic to humans) by the International Agency for Research on Cancer in 2002 [21]. For the classification of carcinogenic PAHs, the 16 priority PAHs were divided into two groups in this study: B2 and Non-B2. The B2 group included the following 8 PAHs: Nap, BaA, BbF, BkF, Chry, BaP, DahA and Ind. The remaining PAHs were classified as Non-B2 compounds. Fig. 3 shows the distributions of the eight carcinogenic PAHs in PM₁₀ from the three sampling sites. 19.67–44.67% of the total PAHs contained in PM₁₀ was human carcinogens, with the highest fraction found in the downtown area, whereas 55.33–80.33% of the total PAHs were not-classified or non-carcinogenic PAHs. Halek et al. reported that seven carcinogenic PAHs (except Nap) accounted for 13.5–23.8% of the total particulate PAHs in Tehran. The fractions of the carcinogenic PAHs identified in Ulsan during the spring and summer periods were about 41–59% higher than those in Tehran [14].

The concentrations of BaP, DahA and eight carcinogenic PAHs (B2) are shown in Fig. 4. The concentrations of BaP, DahA and B2 in ambient PM₁₀ were found to be highest in the downtown area, followed by the industrial area. The levels of BaP from the three sampling sites were relatively higher in late spring compared to those in summer. However, the summer concentrations of the B2 group from the residential and industrial areas were higher than their spring levels. The increased summer level of B2 in the residential area was due to the higher contributions of BbF and BkF, which mainly originated from oil combustion or vehicle emissions [22,23].

3.2. PAH toxicity evaluation

The toxicity equivalent concentrations (TEQs) calculated based on the TEFs values of the PAHs contained in PM₁₀ are shown in Table 5. The TEQs of PAHs in the PM₁₀ samples ranged from 1.74 to 11.55 ng/m³, depending on the sampling area. The late spring TEQs of the PAHs were higher than the summer values. The determined average TEQs values were 6.23, 3.01 and 3.75 ng/m³ in the spring and 5.53, 2.87 and 3.43 ng/m³ in the summer for the downtown, residential and industrial areas, respectively. The mean TEQs of PAHs in the downtown area over the entire study period was much significantly higher than those in the residential and industrial areas. In a comparison of TEQs of PAHs in ambient air with other conducted studies, the TEQs values in Ulsan were higher than those in other cities except for Tianjin, China and Taichung, Taiwan (as shown in Table 6).

Fang et al. indicated that BaP and DahA could be used to identify the carcinogenicity of particle-bound PAHs in central Taiwan [24,25]. Halek et al. reported that BaP was the highest airborne carcinogenic contributor, followed by DahA, Ind and BbF [14]. The average BaP equivalency in PM₁₀ in Ulsan was 1.45 ng/m³, which accounted for 34.81% of the total carcinogenic potency. DahA was also a dominant PAH with regarding to carcinogenic activity, which accounted for 59.39% of the total carcinogenic potency in Ulsan. BaP and DahA should be continuously monitored as major carcinogenic PAHs in the ambient air of Ulsan.

3.3. Effects of seasonal and spatial variations on the toxicities of PAHs

Fig. 5 shows the variations in the TEQs of PAHs in the downtown, residential and industrial areas of Ulsan. The highest average TEQs

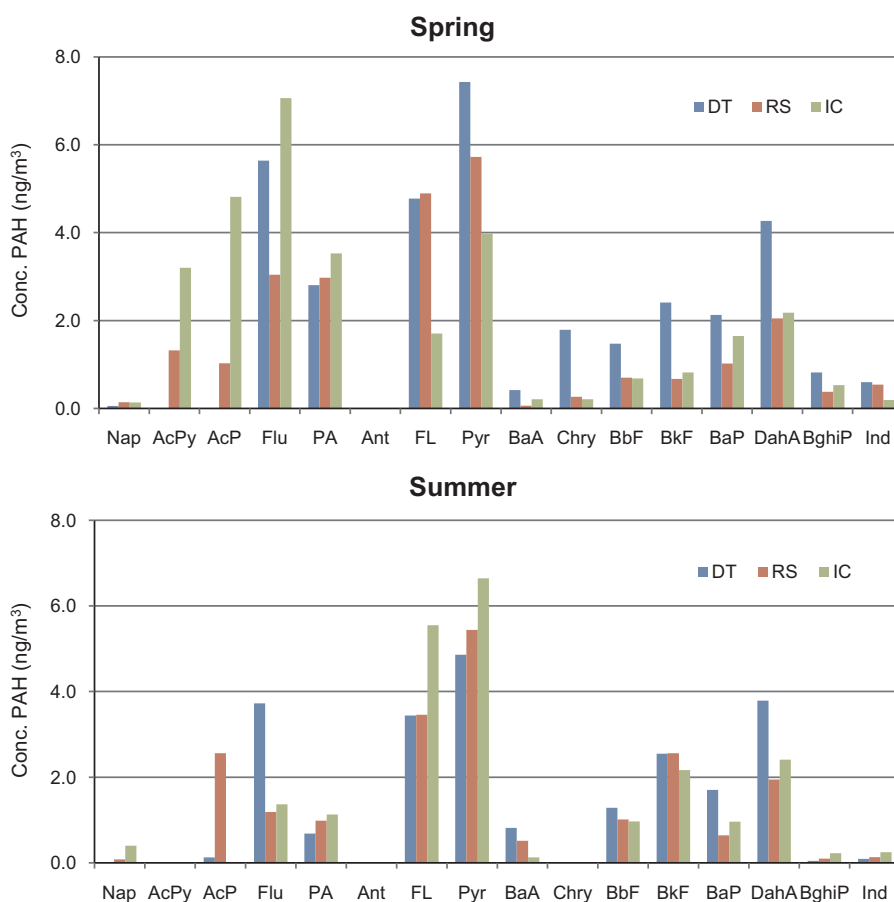


Fig. 2. Concentrations of individual PAHs in airborne PM₁₀ at three sampling sites during spring and summer. DT, downtown; RS, residential area; IC, industrial complex

of PAHs in both seasons were identified in the downtown area, followed by the industrial area. In particular, the average of the TEQ value of PAHs in PM₁₀ from the downtown area was 2.01 and 1.65 times higher than those from the residential and industrial areas, respectively. Characteristics of PAH emission sources, such as local mobile and stationary emissions, have a great effect on the concentrations of PAHs, leading to the variations in TEQs [27,28]. In this study, the downtown area was greatly affected by traffic emissions. In addition, the downtown area was affected by industrial emissions because this area was located in downwind side of the industrial areas. Thus, the concentrations of PAHs in the downtown area, affected by both industrial and vehicle emissions, were much

higher than those in the industrial and residential areas, resulting in the highest TEQs of PAHs occurred in the downtown area. The variation in PAH emission sources can also lead to the changes in the TEQs from different sites. Fang et al. reported that a higher BaP concentration in an urban site with a high traffic volume mainly contributed to increase TEQs [25].

The TEQs of PAHs in the PM₁₀ of Ulsan in the spring were higher than those in the summer season. This situation was mainly associated with decreases in BaP and DahA (except in the IC area) concentrations in the summer compared to those in the spring. The Office of Environmental Health Hazard Assessment (OEHHA, 1994) reported that the lower BaP concentrations in summer peri-

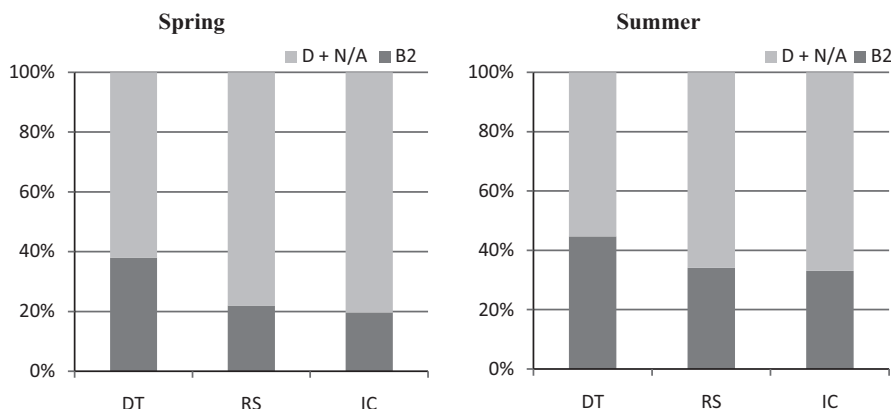


Fig. 3. Concentration distribution of eight carcinogenic PAHs among the 16 priority PAHs determined by the US EPA. Note: B2: 8 carcinogenic PAHs; D+N/A: not classified and non-carcinogenic PAHs; DT, downtown; RS, residential area; IC, industrial complex.

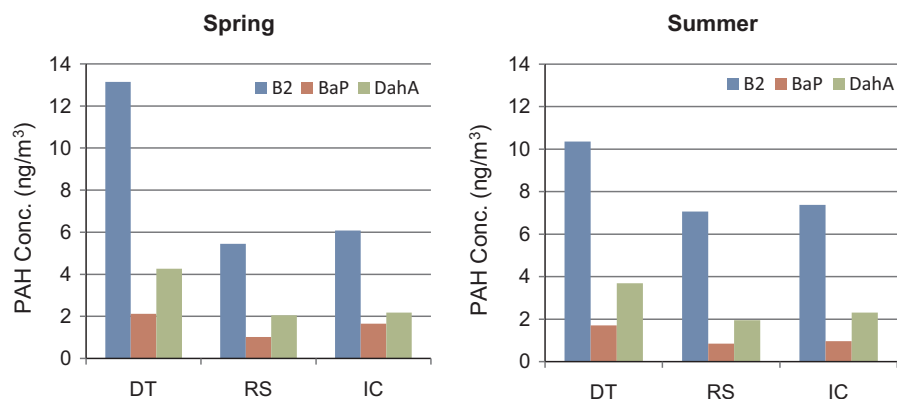


Fig. 4. Concentrations of BaP and eight carcinogenic PAHs. B2: The group contains carcinogenic PAHs. DT, downtown; RS, residential area; IC, industrial complex.

Table 5
Toxicity equivalency concentrations (TEQs) of PAHs (ng/m^3).

	Late spring			Summer		
	DT	RS	IC	DT	RS	IC
Nap	0.000	0.000	0.000	0.000	0.000	0.000
AcPy	0.000	0.001	0.003	0.000	0.000	0.000
AcP	0.000	0.001	0.005	0.000	0.003	0.000
Flu	0.006	0.003	0.007	0.003	0.001	0.001
PA	0.002	0.002	0.002	0.000	0.001	0.001
Ant	0.000	0.000	0.000	0.000	0.000	0.000
FL	0.005	0.005	0.002	0.003	0.003	0.005
Pyr	0.007	0.006	0.004	0.005	0.005	0.007
BaA	0.006	0.001	0.003	0.011	0.007	0.002
Chry	0.047	0.007	0.005	0.001	0.000	0.000
BbF	0.162	0.077	0.075	0.141	0.112	0.106
BkF	0.089	0.025	0.030	0.094	0.095	0.080
BaP	2.126	1.021	1.649	1.901	0.913	1.064
DahA	3.797	1.824	1.941	3.373	1.730	2.144
BghiP	0.010	0.004	0.006	0.000	0.000	0.003
Ind	0.040	0.036	0.013	0.000	0.002	0.017
Total	6.297	3.013	3.746	5.332	2.802	3.430

DT, downtown; RS, residential area; IC, industrial complex.

Table 6
Comparison TEQs (ng/m^3) of PAHs in PM_{10} between Ulsan and other cities.

Cities	PAHs	TEQs (ng/m^3)	References
Ulsan, Korea	16	4.15	This study
Beijing, China	17	3.67	[23]
Tianjin, China	17	25.8	[23]
Seoul, Korea	13	3.87 ^a	[24]
Bangkok, Thailand	9	3.73 ^a	[24]
Tehran, Iran	7	2.84–7.65	[14]
Taichung, Taiwan	20	5.26	[25]
Zaragoza, Spain	20	1.0–3.0	[26]

^a TEQs (ng/m^3) of PAHs in gas and particle phase.

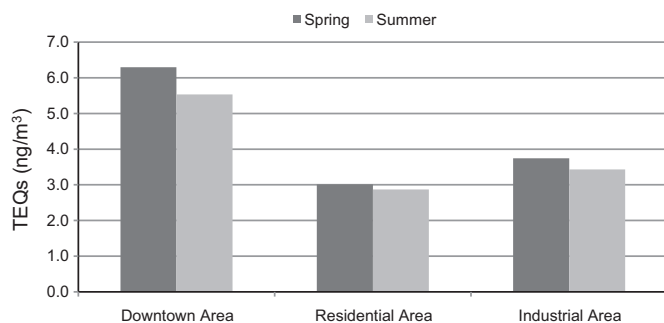


Fig. 5. Toxicity equivalency concentrations (TEQs) of the total PAHs in PM_{10} .

ods were due to the short lifetime of BaP in the atmosphere during the hot season [29].

Fig. 6 represents the relationship between total PAH concentrations and TEQs in each studied area of Ulsan over the entire study period. The PAH concentrations had a strong positive relationship with TEQs, whose squared correlation coefficient (r^2) ranged from 0.73 to 0.90, depending on the season and location. The highest r^2 between TEQs and total PAH concentrations was found in the residential area ($r^2 = 0.72$, $p < 0.01$), followed by those of the residential area ($r^2 = 0.70$, $p < 0.01$) and the downtown area ($r^2 = 0.69$, $p < 0.01$). The overall correlation coefficient (r^2) between TEQs and total PAH concentrations from all three sampling sites was 0.57 ($p < 0.01$), much lower than those of the individual sites, possibly due to complicated interactions among many different PAH emission sources [30].

3.4. Relationships between the TEQs of PAHs and other pollutants or meteorological parameters in ambient air

Table 7 shows the statistical relationships based on the analysis using an SPSS package (version 16.0), between the TEQs of PAHs in PM_{10} and the concentrations of other air pollutants, such as SO_2 , NO_2 , O_3 and PM, and meteorological parameters in the ambient air during the spring and summer study periods.

In the spring period, the TEQs of PAHs in PM_{10} had a significant correlation with the concentrations of particulate matter.

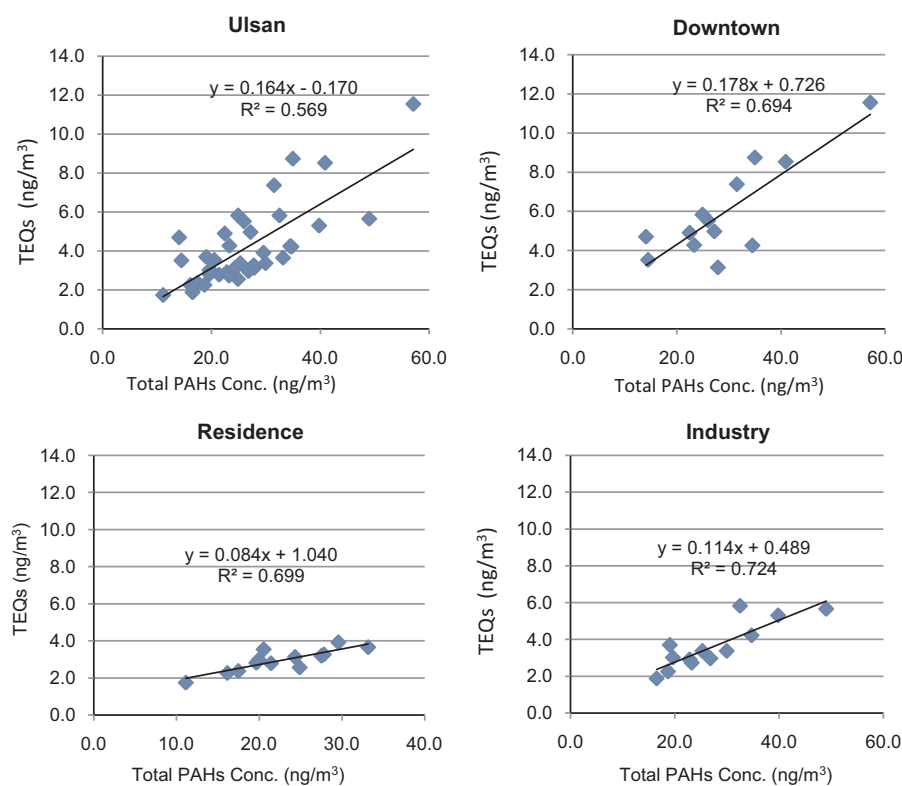


Fig. 6. Correlations between PAH concentrations and TEQs.

Table 7

Correlation between TEQs and air pollutants and meteorological parameters.

	SO ₂	NO ₂	O ₃	PM _{2.5}	PM ₁₀	CO	Temp	WS	RH	TEQs
(a) Spring										
SO ₂	1									
NO ₂	0.89**	1								
O ₃	-0.57**	-0.58**	1							
PM _{2.5}	0.57**	0.57**	-0.16	1						
PM ₁₀	0.62**	0.72**	-0.06	0.78**	1					
CO	0.64**	0.72**	-0.24	0.46*	0.44	1				
Temp	-0.12	0.03	0.29	-0.21	-0.03	0.34	1			
WS	-0.48*	-0.56**	0.63**	-0.21	-0.14	-0.54*	-0.30	1		
RH	-0.19	-0.37	-0.05	-0.05	-0.29	-0.45*	-0.58**	0.30	1	
TEQs	0.52*	0.54*	0.02	0.68**	0.76**	0.33	-0.22	-0.01	-0.16	1
(b) Summer										
SO ₂	1									
NO ₂	0.39	1								
O ₃	0.32	-0.16	1							
PM _{2.5}	0.05	0.31	0.23	1						
PM ₁₀	0.43	0.51*	0.43	0.46	1					
CO	0.36	0.60**	0.25	0.48*	0.84**	1				
Temp	-0.37	-0.42	-0.17	-0.39	-0.57*	-0.57*	1			
WS	-0.21	-0.48*	0.13	-0.11	-0.35	-0.59*	0.34	1		
RH	0.61**	0.42	-0.04	-0.02	0.03	0.23	-0.03	-0.47*	1	
TEQs	0.39	0.56*	-0.11	0.43	0.43	0.38	-0.51*	-0.17	0.12	1

Temp, temperature (°C); WS, wind speed (m/s); RH, relative humidity (%).

* Correlation is significant at the 0.05 (2-tailed).

** Correlation is significant at the 0.01 (2-tailed).

The correlation coefficient (r) values were 0.68 and 0.76 for PM_{2.5} and PM₁₀ ($p < 0.01$), respectively. The TEQs also showed significant correlation with the concentrations of SO₂ ($r = 0.54$, $p < 0.05$), NO₂ ($r = 0.52$, $p < 0.05$) and CO ($r = 0.42$, $p < 0.05$). The relatively high correlation of PAHs and particulate PAHs with NO₂ concentration illustrates that NO₂ and particulate PAHs have some similar local emission sources such as traffic emissions. A positive relationship between the TEQs and SO₂ concentrations suggests that the concentrations of carcinogenic PAHs and SO₂ are affected by the similar

industrial emission sources, such as combustion of fuel or waste [31].

During the summer period, however, the TEQs showed a significant correlations only with NO₂ ($r = 0.56$, $p < 0.05$) and temperature ($r = -0.51$, $p < 0.05$). The summer TEQs and temperature showed a negative correlation. This may represent that some toxic PAHs, such as BaP, are photochemically decomposed during hot summer periods. The BaP concentrations during the summer season showed much lower than those during the spring season (Fig. 4).

These results could be explained by the degenerative photoreactions between PAHs and other pollutants or by the volatilization of some PAHs under sunny conditions. PAHs can react with other air pollutants, such as O₃, SO₂ and NO₂, resulting in the formations of hydroxyl-PAHs, sulfur-PAHs and nitro-PAHs, respectively [9]. Even though PAHs and these pollutants might be derived from similar sources, they could expose to very complex atmospheric reactions. In particular, the lower correlations can be explained by the differences in chemical or photochemical reactions, atmospheric deposition, and transport pathways, may depend upon different diurnal source patterns that can lead to variations in air pollutant concentrations. SO₂ concentrations greatly decreased during the summer sampling period as compared to those during the spring one. However, the reduction trends in concentration of SO₂ and PAHs, such as BaP, were quite different from each sampling site. Therefore, any significant correlations between TEQs and SO₂ were not found in the summer. The total TEQ of PAHs from the three sampling sites showed significant correlations with the air pollutants during the entire period of study as follows: NO₂ ($r=0.52$, $p<0.01$), PM_{2.5} ($r=0.53$, $p<0.01$), PM₁₀ ($r=0.65$, $p<0.01$).

4. Conclusions

The concentrations of 16 priority PAHs in PM₁₀ and their toxicity in three sampling areas of Ulsan were identified during the late spring and summer periods. The average spring concentration of 30.10 ± 10.49 ng/m³ of total PAHs in PM₁₀ in Ulsan was higher than the summer concentration of 21.93 ± 6.64 ng/m³. The TEQ of PAHs was found to be highest in the downtown area, followed by that of the industrial area. BaP and DahA were the major PAHs which contribute to the TEQs of PAHs in PM₁₀. The decrease of BaP concentrations during the summer period may be a cause of the lower TEQs as compared than those during the late spring period. The characteristics of the PAH sources greatly affected the concentrations and their toxicity of the PAHs.

A strong correlation was found between the TEQs and concentrations of total PAHs in PM₁₀. The TEQs significantly correlated with the levels of air pollutants (PM, SO₂, NO₂ and CO), depending on the seasons. The TEQs showed a negative significant correlation with temperature in the summer periods.

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