Journal of Hazardous Materials 175 (2010) 540–550

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Effects of road characteristics on distribution and toxicity of polycyclic aromatic hydrocarbons in urban road dust of Ulsan, Korea

Byeong-Kyu Lee*, Trang T.T. Dong

Department of Civil and Environmental Engineering, University of Ulsan, Ulsan 680-749, Republic of Korea

ARTICLE INFO

Article history:
Received 12 August 2009
Received in revised form
21 September 2009
Accepted 12 October 2009
Available online 24 October 2009

Keywords:
PAHs
Pavement
Vehicle speed
Traffic density
Toxicity

ABSTRACT

Comparisons between concentration, size effect, molecular distribution, and toxicity of polycyclic aromatic hydrocarbons (PAHs) in urban road dust of Ulsan, Korea, were carried out. The road dust was collected at eleven representative urban sites offering unique road characteristics. The road dust was separated into four size categories as follows: 850–2000 μm, 180–850 μm, 75–180 μm and less than 75 μm. PAHs in the categorized road dust were ultrasonically extracted by a mixture of dichloromethane and *n*-hexane (1:1) for 30 min. Sixteen PAHs were specifically identified by a high performance liquid chromatography method. Pavement type, traffic volume, vehicle speed and surrounding environment of the study roads greatly affected the overall PAH road dust concentration. The molecular distribution of PAHs was strongly affected by vehicle type, surrounding area and pavement type of road. When the road dust particle size decreased, the total concentration of PAHs increased. The existence of coarse asphalt particles due to the abrasion of new asphalt pavement at some sites could increase the total PAH concentration to a size of 180–850 μm. PAHs in road dust were also evaluated for toxicity using the reported toxicity equivalency factors. The toxicity of PAHs in road dust showed a strong correlation to the total PAH concentration (r^2 = 0.955). However, the coefficients of determination (r^2) for the sizes of 850–2000 μm, 180–850 μm, 75–180 μm and less than 75 μm were 0.966, 0.998, 0.707 and 0.514, respectively.

1. Introduction

Vehicle emissions are a significant and complex source of pollutants within urban areas. Motor vehicles account for approximately 36% of the total yearly emission of polycyclic aromatic hydrocarbons (PAHs) in the United States [1]. PAHs are widespread organic pollutants containing two or more aromatic rings that are fused together in different arrangements [2]. Since many PAHs and their derivatives are considered to be carcinogenic and/or mutagenic compounds, they have been a great cause of concern for environmental scientists in recent years [3–8]. Anthropogenic PAHs are usually generated from incomplete combustion of gasoline, diesel and other types of fuel which are used in many processes including automobiles and engines operation, domestic cooking and heating systems, refuse burning and various industrial activities [2,9–13]. Because of the significant contribution of vehicle emissions to PAHs within the atmosphere, road dust has a high potential for containing these compounds. It has been reported that vehicle exhausts, lubricating oils, weathered materials of road surfaces, tire particles, asphalt pavement, construction materials, and atmospherically deposited materials are responsible for PAH concentration in the surface of road dust within urban areas [7,8,14–16]. Also, it has been confirmed that diesel vehicle exhaust, tire abrasion and pavement are major contributors of PAHs in road dust in Japan [16]. The mixing effect of traffic emission and coal combustion was demonstrated as the main source of PAHs in road dust in central Shanghai, China. PAHs in road dust can affect human health as well as the ecosystem when road dust is dispersed into the air under wind effects and washed off into the aquatic environment during the rainy season [15,17–19]. It has been confirmed that 28% of fine-sized aerosol within the atmosphere originates from road dust, while 57% of coarse size fractions originate from road dust [20]. Hoffmann et al. [19] estimated that 36% of environmental PAH input was due to urban runoff. Urban runoff has been recognized as an important PAH pathway to water environments and aquatic ecosystems [21]. Due to the strong effects of PAHs in air and water environments, road dust has become a great concern in recent research.

The concentration of PAHs within road dust was assumed to be influenced by traffic density and the deposition rate of atmospheric particulate matter [3]. Butler et al. [22] and Li et al. [23] also found that PAH concentrations within road dust varied by the distance from the sources of pollution. The purpose of this study was to analyze the effect of road characteristics on the concentrations and toxicities of PAHs found in road dust. This study identified characteristics of PAHs in road dust collected from roads with vary-

* Corresponding author. Tel.: +82 52 259 2864; fax: +82 52 259 2629.
E-mail address: bklee@ulsan.ac.kr (B.-K. Lee).

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.10.039

Table 1
Summary of the characteristics of road dust sampling sites.

Category of road	Characteristic	Sampling site
Pavement type	Concrete	1
	Asphalt	2
Traffic density	High (rotary 1, 2, 3)	3, 4, 5
	Low (residential 1, 2, 3)	6, 7, 8
Fraction of diesel vehicle	Higher	9
	Lower	10
Vehicle speed	Low	11
	Medium	10
	High	2
Surrounding area	Typical urban residential	6
	Industrial residential	8

ing conditions, vehicle movements and environments. Investigated roads were categorized based on their pavement materials, traffic density, vehicle types, vehicle speed and characteristics of the surrounding area.

2. Materials and methods

2.1. Sampling site description

Ulsan is a representative industrial city with the largest petrochemical industrial complex (IC), non-ferrous metallic IC, mechanical and shipbuilding IC of Korea (Fig. 1). This city has a population of more than 1.1 million as well as wide coastal areas. The feature of airborne pollutant emissions for this city is quite different from other cities in Korea due to the high emission contribution from industries. Industrial and vehicle emissions are responsible for 56% and 18% of the total air emissions in Ulsan, respectively, when compared with 27% and 41% of them in South Korea [5].

Eleven sites representing different characteristics of road and traffic were chosen for comparison (Fig. 1). The characteristics of each selected road are categorized and summarized in Table 1:

- Types of pavement: Sites 1 and 2 are representative of both a concrete and asphalt road, respectively. These two sites are located along the same highway of Ulsan, thus they have the same traffic density.
- Traffic volume: Sites 3–8 are representative of two road categories in terms of traffic density. Sites 3–5 are rotary areas which have a relatively high traffic density with an average of 33,570 vehicles per day in comparison to sites 6–8 in residential areas with an average of 8480 vehicles per day.
- Different fractions of diesel vehicles: Site 9 represents a road whose diesel vehicle fraction is higher than that of site 10. The fractions of diesel and gasoline vehicles at site 9 are 33.1% and 67.9%, respectively, while they are 18.2% and 81.8% at site 10, respectively.
- Vehicle speed: There are three categories of road in terms of vehicle speed. Sites 11, 10 and 2 represent roads with low, medium and high vehicle speeds, respectively.
- Surrounding area: Two residential sites numbered 6 and 8 were chosen for a comparison between the urban residential area and the industry-nearby residential area. Site 6 is a typical urban residential area in that it is remote from industrial areas. Meanwhile, site 8 is also a residential area but it is located near the petrochemical IC and the non-ferrous metallic IC.

2.2. Sample collection and preparation

Road dust samples were collected using a vacuum cleaner equipped with a 15 cm × 15 cm × 15 cm filter pack in March of 2006. An approximate amount of 500 mg of road dust sample was collected from each sampling site along approximately a 100 m length and 0.3 m width of both sides of each road. After sampling was complete, the entire filter pack containing the road dust was put into a sealed plastic bag and transported to the laboratory for sample pre-treatment and analysis.

Road dust samples were spread out into a height of less than 0.5 cm in a clean room with conditions of 20 ± 1 °C and 40 ± 5%RH and were dried at room temperature for seven days before being

Fig. 1. A map of the road dust sampling sites in Ulsan.

Table 2
Sixteen PAHs classified by molecular weight and cyclic ring number.

Low MW PAH	Ring #	Medium MW PAH	Ring #	High MW PAH	Ring #
Naphthalene (NaP)	2	Fluoranthene (FL)	4	Benzo(*b*)fluoranthene (BbF)	5
Acenaphthylene (AcPy)	3	Pyrene (Pyr)	4	Benzo(*k*)fluoranthene (BkF)	5
Acenaphthene (Acp)	3	Benzo(*a*)anthracene (BaA)	4	Benzo(*a*)pyrene (BaP)	5
Fluorene (Flu)	3	Chrysene (CHR)	4	Dibenzo(*a*,*h*)anthracene (DBA)	5
Phenanthrene (PA)	3			Benzo(*g*,*h*,*i*)perylene (BghiP)	6
Anthracene (Ant)	3			Ideno(1,2,3-cd)pyrene (IND)	6

Note: MW stands for molecular weight.

manually filtered through a 2 mm sieve in order to remove larger particles as well as any impurities. Three stainless steel sieves with screen sizes of 850 μm, 180 μm and 75 μm were used to separate the road dust particles with a diameter of less than 2 mm into four particle sizes as follows: 850–2000 μm, 180–850 μm, 75–180 μm, and less than 75 μm. The four categorized particle sizes of road dust samples were weighed in order to identify their size fractions. The weight fraction of each size was identified as the ratio of its weight to the total weight of all four sizes. The road dust samples were stored separately in zip-loc bags in a desiccator.

2.3. PAH extraction and analysis

Prepared road dust samples were put in a desiccator for 48 h in order to minimize weight errors due to varying moisture levels. Road dust samples conditioned in desiccators were homogenized by mixing with a stainless steel spatula for more than 5 min. Road dust samples weighing 2 g were stored within a vial and extracted with a mixture of *n*-hexane and dichloromethane (DCM), with a volume ratio of 1:1 in an ultrasonic bath (Branson 1210 Sonic bath) for 30 min at room temperature around 20 °C [24,25]. Then, the extract was filtered through a 5B Advantec filter paper and was concentrated to 2 ml by use of a Sibata BIP-1200 nitrogen concentrator. The concentrated solution was sent for PAHs analysis using a high performance liquid chromatograph (HPLC) with the Chromspher 5 PAH 4.6 mm (ID) × 150 mm (L) column and a 310 UV detector at 260 nm. A mixture of acetonitrile (ACN) and water was used as the mobile phase with a solvent gradient method and a flow rate of 1.0 ml/min at 35 °C. Sixteen PAHs included in the US Environmental Protection Agency list were analyzed as shown Table 2: naphthalene (Nap); acenaphthylene (AcPy); acenaphthene (Acp); fluorene (Flu); phenanthrene (PA); anthracene (Ant); fluoranthene (FL); pyrene (Pyr); benzo(*a*)anthracene (BaA); chrysene (CHR); benzo(*b*)fluoranthene (BbF); benzo(*k*)fluoranthene (BkF); benzo(*a*)pyrene (BaP); dibenzo(*a*,*h*)anthracene (DBA); benzo(*g*,*h*,*i*)perylene (BghiP); and indeno(1,2,3-cd)pyrene (IND).

The PAHs in road dust were identified by comparing their retention times with those of standard solutions. The linearity for quantification analysis of each PAH was identified by using the peak areas of six concentration levels (5 ppm, 10 ppm, 20 ppm, 40 ppm, 100 ppm, and 200 ppm) of standard PAHs. The relative standard deviations (RSD%) and linear regression coefficients (R^2) of the 16 analyzed PAHs were reported in the sister's paper of this study [26]. The RSD% of nearly all PAHs, with the exception of Nap, PA, Ant, and CHR, were below 4.7%. Most PAHs had a R^2 of nearly 1.0 (greater than 0.996) with exception of Ant having R^2 of 0.962. However, the Ant identified in our road dust samples showed a concentration range of 0–20 ppm, and its linearity having R^2 value of 0.994 was almost similar to those for most of the PAHs.

QA/QC procedures for analysis of PAHs were referred by the methods reported by Bi et al. [26]. The PAHs were not detected in the solvent blanks used for extraction of the PAHs in the road dust samples. A surrogate spike mix of deuterated standard PAHs, Sigma 4-8935, including naphthalene-d8, acenaphthalene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12, was added to the extracts before the HPLC analysis in order to check the recovery rates [27]. Surrogate compounds were consistent with the analysis as follows: naphthalene-d8 for Nap; acenaphthalene-d10 for AcPy, Acp and Flu; phenanthrene-d10 for PA, Ant, FL and Pyr; chrysene-d12 for BaA and CHR; perylene-d12 for BbF, BkF, BaP, DBA, BghiP and IND. The recovery rates of the deuterated PAHs (surrogate compounds) ranged from 75% to 112%. These recovery rates were then used to correct the concentrations of the PAHs in the road dust samples. However, this study did not identify the extraction efficiencies of the PAHs from the road dust samples. This study just assumed that most of the PAHs included in the road dust were completely extracted in the extraction solvent. Thus some errors concerned concentration evaluation of the PAHs, particularly Nap having relatively high vapor phase at room temperature, in road dust may be involved.

2.4. Toxicity evaluation method

Some PAHs, such as Nap, BaA, BbF, BkF, BaP, and DBA, have been known to be mutagenic and/or carcinogenic compounds [29]. The toxicities of the PAHs identified in the road dust samples were evaluated using a relative toxicity value of each PAH compound. The PAH toxicities of the road dust samples were calculated based on the set of toxicity equivalency factors (TEFs) of PAHs proposed by Nisbet and LaGoy [30]. BaP considered as the most toxic PAH was utilized as the reference chemical by several authors [29–32] and was assigned a value of 1 in the TEF system. Other PAHs have their own TEF values based on their carcinogenic level in comparison to that of BaP as reported in the previous papers [28,30]. The toxic equivalent concentration (TEQ) of each road dust sample was obtained by summing the products of each individual PAH concentration and its TEF, as follows:

$$\mathrm{TEQ} = \sum (C_i \times \mathrm{TEF}_i)$$

where, TEQ is the toxic equivalent concentration, C_i is the concentration of PAH I, and TEF_i is toxicity equivalency factor of PAH i.

3. Results and discussion

3.1. PAH concentration distribution

The individual and overall concentrations of each PAH in the road dust of Ulsan are presented in Table 3. The individual concentrations were obtained by summing the products of the PAH concentrations identified for each particle size and its weight fraction. The overall concentrations of PAHs shown in Table 3 represent the sum of the individual concentrations for 16 PAHs. The overall PAH concentration of road dust ranged from 19.69 μg/g to 154.64 μg/g. The greatest PAH concentration was obtained at a rotary, which had the highest traffic density of the roads studied, while the lowest concentration was identified in a typical urban residential area. Nap, BaA, CHR and BbF were not detected in most of the samples. BkF had the highest concentration in comparison to

Table 3
Individual and overall concentrations of each PAH in road dust (unit: μg/g).

Site	1	2	3	4	5	6	7	8	9	10	11
Nap	ND	ND	ND	ND	ND	ND	0.06	ND	0.03	ND	ND
AcPy	ND	0.08	ND	1.49	0.09	ND	0.28	ND	ND	ND	ND
Acp	0.42	ND	3.14	2.36	0.40	0.18	2.51	1.32	1.73	ND	0.48
Flu	0.16	0.08	0.76	0.98	0.34	0.19	0.54	0.37	0.19	0.06	0.23
PA	0.23	1.85	0.53	0.76	1.64	0.10	0.66	1.47	0.13	0.11	0.28
Ant	0.17	0.43	0.45	0.35	0.24	0.06	0.50	0.16	0.14	0.06	0.16
FL	5.06	5.20	20.69	4.51	6.91	2.56	7.07	5.67	5.03	11.11	7.14
Pyr	10.37	6.55	18.27	10.02	1.89	2.12	8.38	7.77	15.65	11.63	9.36
BaA	ND	0.30	ND	ND	ND	ND	ND	ND	ND	ND	ND
CHR	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BbF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BkF	19.79	6.76	36.51	22.24	11.49	10.07	14.44	12.72	14.90	21.04	19.67
BaP	1.91	2.68	19.23	9.36	3.31	2.42	4.97	5.56	5.76	7.92	6.32
DBA	10.32	4.73	21.85	1.74	11.93	0.87	2.95	7.11	1.37	9.80	3.60
BghiP	6.78	10.62	15.06	13.34	15.52	0.46	2.76	26.56	4.58	8.88	3.47
IND	7.77	1.15	18.15	ND	ND	0.67	3.71	ND	ND	2.74	1.76
Overall	62.98	40.44	154.64	67.15	53.76	19.69	48.83	68.73	49.50	73.35	52.45

ND: not detected. 1: Concrete highway; 2: asphalt highway (or high-speed road); 3: rotary 1 at highway end; 4: rotary 2 at downtown; 5: rotary 3 at riverside; 6: typical urban residential area; 7: new developed residential area; 8: nearby-industry residential area; 9: low-diesel road; 10: high-diesel road, medium-speed; 11: low-speed road.

other PAHs, except in the sample from site 9. The concentration of BaP, used as an indicator of reference toxicity, in road dust ranged from 1.91 μg/g to 19.23 μg/g. The highest and lowest BaP values were obtained at the rotary (having the highest traffic density) and the concrete highway, respectively. The following sections were analyzed in terms of concentration, size distribution and molecular distribution of PAHs identified from road dust with different road characteristics. Sixteen PAHs were classified into five groups based on the number of aromatic rings in the PAH compounds as follows. The 2-ring group included Nap, the 3-ring groups included AcPy, Acp, Flu, PA and Ant, the 4-ring group was made up of FL, Pyr, BaA and CHR, the 5-ring group included BbF, BkF, BaP and DBA, and the 6-ring groups was composed of BghiP and IND. As shown in Table 2, the 16 PAHs can be also classified into three groups depending upon their molecular weight (MW) such as low MW PAHs (with 2- or 3-ring), medium MW PAHs (with 4-ring) and high MW PAHs (with 5- or 6-ring).

3.1.1. Effect of pavement type

Fig. 2a–c compares the PAH characteristics in road dust obtained from a concrete highway and an asphalt highway with the same traffic volumes and vehicle speeds.

The size distribution pattern of the total PAH concentration from the concrete highway was quite different from that of the asphalt highway (Fig. 2a). Smaller size of road dust, which has more surface area available for PAH exposure, usually shows higher concentration of PAHs than lager one. However, in the asphalt highway road dust, the PAH concentration in the 850–2000 μm-sized particles was higher than in those with a size of 180–850 μm. The reason behind this phenomenon may be due to the existence of asphalt particles or debris in the size category of 850–2000 μm. This phenomenon also occurred in other roads with new asphalt pavement (see Section 3.2). For the concrete highway, the road dust with a size of 180–850 μm showed a greatly elevated PAH concentration in comparison to other types of road dust. This may be due to the high weight fraction of tire particles in this size category. Tire particles may more commonly occur due to the high level of abrasion caused by the roughness of concrete pavement. The PAH concentrations for each particle size category in the road dust from the asphalt highway were much higher than those from the concrete highway, except in the size of 180–850 μm. Even though the road dust from the asphalt highway had a much higher PAH concentrations within three particle size groups (850–2000 μm, 75–180 μm, and less than 75 μm), its overall PAH concentration was lower. The PAH concentration for a dominant particle group of road dust can greatly affect the overall PAH concentration. The dominant particle weight group was in the size range of 180–850 μm for road dust, making up their weight fractions of 52.2% and 77.3% to the weight of the road dusts obtained from the concrete and the asphalt highways, respectively. The PAH concentration for the dominant size group of the asphalt highway road dust was much lower, resulting in overall lower concentrations of PAHs in comparison to those from a concrete highway.

The overall PAH concentration from the concrete highway (63.0 μg/g) was 1.5 times higher (42.4 μg/g) than that of the asphalt highway (Fig. 2b). This fact infers that a concrete highway is more abrasive upon tires causing them to break down and release small particles, resulting in an increased PAH concentration in comparison to an asphalt highway.

Naphthalene was not detected in either type of highway road dust. This fact might be referred to methodology where naphthalene has low molecular weight (2-ring) and evaporated at low temperature during sampling, drying and extraction processes. Also, this study did not analyze the vapor phase of Nap and thus it could result in lowering Nap concentration or not being detected Nap. The major PAHs that formed in both highway road dusts were 5-ring PAHs which occupied 50.8% and 35.1% of the overall PAH concentration in the concrete and asphalt highways, respectively (Fig. 2c). The concentration fraction of 3-ring PAHs, such as Flu, PA and Ant, in the road dust from the asphalt highway was 6.0%, which was higher than the 1.6% from the concrete highway. Recently, Boonyatumanond et al. [4] reported that the PA and Ant fractions, with respect to the PAH concentration of asphalt samples, were 12.7% and 2.1%, respectively. The PA and Ant fractions in the asphalt sample were higher, with fractions of 8.0% and 1.2%, respectively, from those of normal street dust. Thus, the reason for the higher fraction of 3-ring PAHs in the road dust from the asphalt highway than that of the concrete highway is due to the higher concentration of PA and Ant within the asphalt components.

3.1.2. Effect of traffic volume and fuel

Fig. 3a–c shows the overall distribution for PAH concentration, the PAH concentration for different particle sizes, and the molecular distribution of PAHs, respectively, for road dust occurring in heavy traffic rotary areas and residential areas.

In a comparison of total PAH concentration for different particle sizes of road dust, the highest concentration was obtained for the

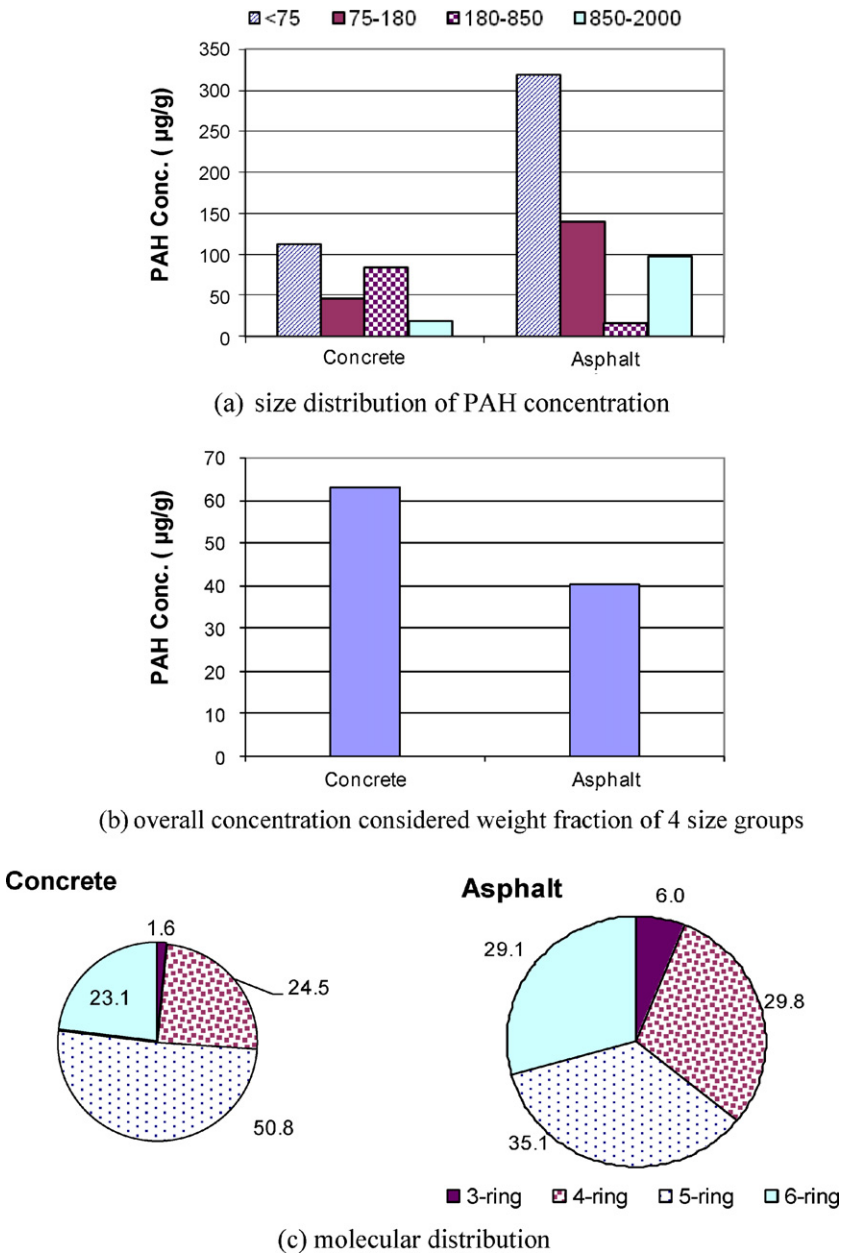


Fig. 2. Concentrations of PAHs in road dust from concrete and asphalt roads.

smallest size (i.e., less than 75 μm) followed by the size group of 75–180 μm (Fig. 3a). The total PAH concentration increased when the particle size decreased. This trend was due to the relatively higher areas of exposure for the smaller sized particles for the case of road dust from concrete and asphalt roads. However, for the case of road dust at residential site 3, the total PAH concentration for the coarse particles (850–2000 μm) was higher than that of the smaller sized particles (180–850 μm). This phenomenon may be due to the coarse asphalt particles derived from the new asphalt pavement of the road, as discussed in the previous section (Fig. 2a). The molecular distribution patterns among heavy traffic rotary areas were similar (Fig. 3). This fact illustrates that there is a similarity of PAH emission sources within the traffic rotary areas. However, the distribution patterns of PAHs among residential areas having different surroundings significantly varied.

The overall average of PAH concentrations in heavy traffic rotary areas was two times higher than that of urban residential areas (Fig. 3b). The overall average of PAH concentrations in high traffic rotary and residential areas of Ulsan were 91.85 μg/g and 45.75 μg/g, respectively, which were much higher than the values reported in Taichung, Taiwan and Shanghai, China. Fang et al. [11] reported that the PAH concentration for roadside dust was 65.8 μg/g and 16.1 μg/g for traffic roads and background areas, respectively. The PAH values for road dust measured at traffic and residential areas in Shanghai, China were 18.8 μg/g and 12.4 μg/g, respectively [14]. It was a little difficult to get real urban background samples of road dust in Ulsan. This study assumed the road dust, which was collected from a residential area located in a suburban-rural area, could be a role as a background. The background road was located in a remote area from industrial areas and did not have much road traffic. The identified PAH concentration of the background road dust was 19.49 μg/g. This represents that traffic activities in Ulsan greatly increased the concentrations of PAHs in the road dusts.

The traffic volume in the rotary areas in Ulsan was much higher than those in the referred study areas. Thus, the high concentrations

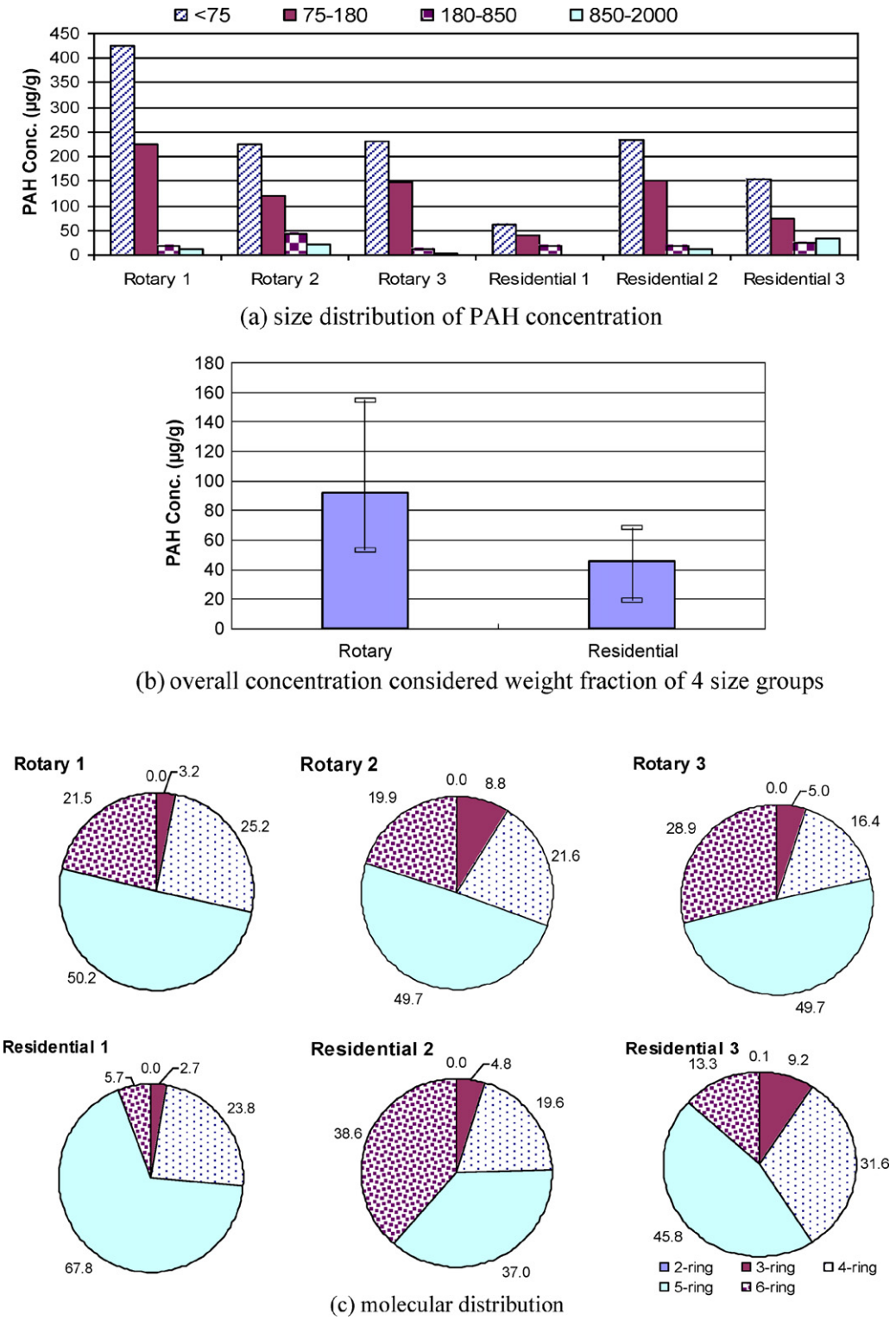


Fig. 3. Concentrations of PAHs in road dust in rotary and residential areas.

identified in this study suggest that the traffic volume or vehicle operation in Ulsan has great effects upon the PAH concentration in the road dust. This fact is consistent with the results of other studies [3,11,14].

In comparison of the molecular distribution of PAHs as shown in Fig. 4, the high-diesel road, with diesel vehicle passing of 33.1%, had higher ratios of PAHs with 3- and 4-rings, 4.4% and 41.8%, respectively. However, their concentration fractions of 3- and 4-rings of PAH in the low-diesel road, with diesel vehicle passing of 18.2%, showed 0.8% and 31.0%, respectively. These results were consistent with previously reported results [33,34]. On the contrary, because of its higher fraction of gasoline vehicles in comparison to the high-diesel road, the low-diesel road had higher ratios of the PAHs with 5- and 6-membered rings, which are emitted with more abundance

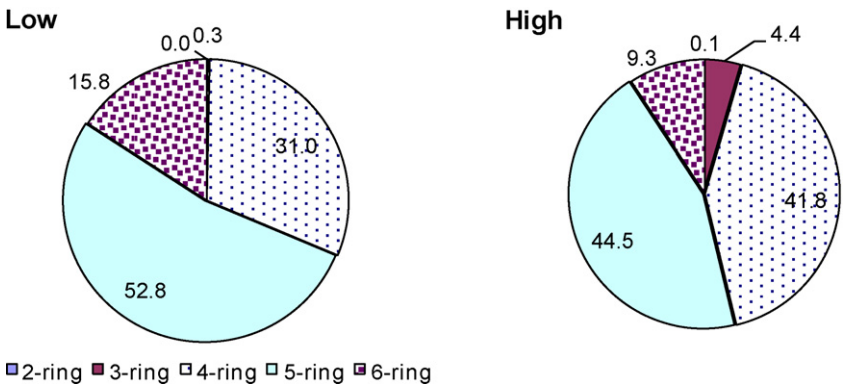
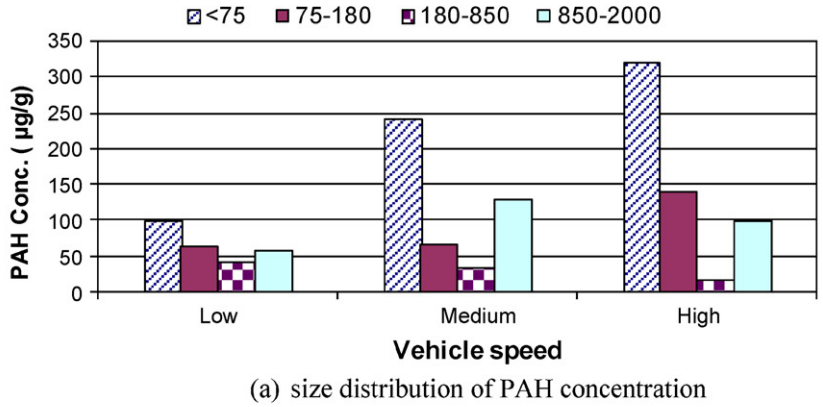
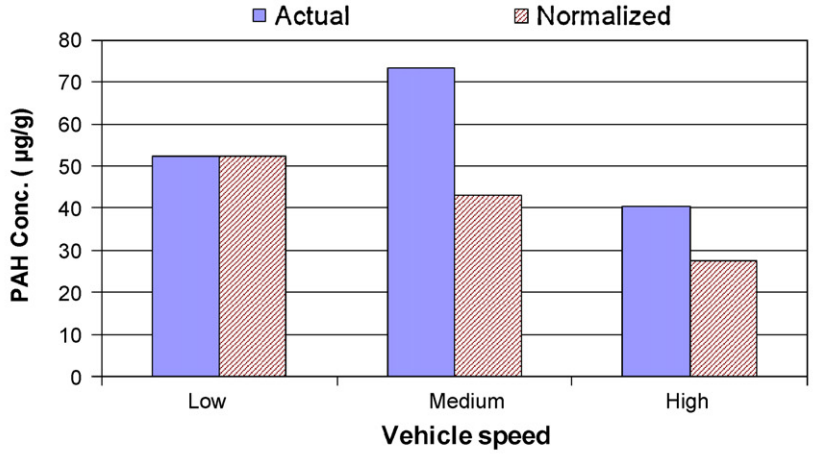


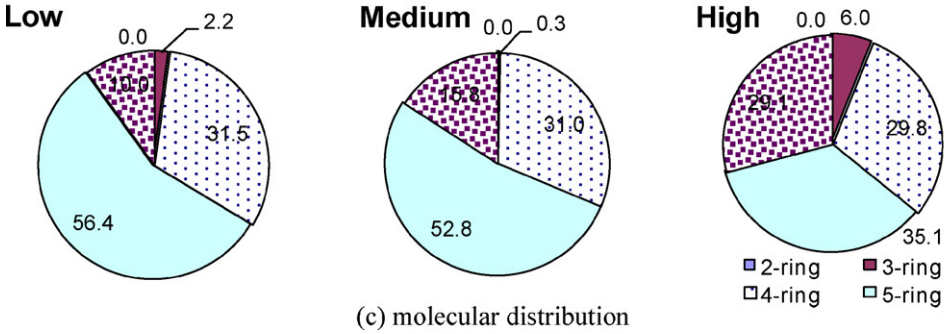
Fig. 4. Molecular distribution of PAH concentrations in road dust from roads with a different fraction of diesel vehicles.



(a) size distribution of PAH concentration



(b) overall concentrations (measured vs normalized with the same traffic volume)



(c) molecular distribution

Fig. 5. Concentrations of PAHs in road dust from roads with different vehicle speeds.

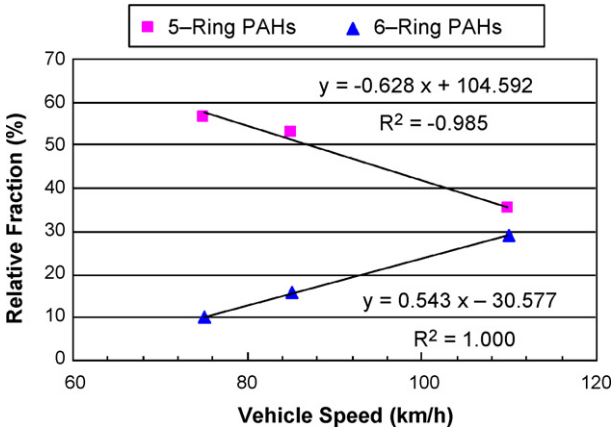


Fig. 6. Correlation between vehicle speed and relative fraction of PAHs with 5- and 6-membered rings.

from gasoline engines rather than from diesel ones [12,35]. The differences in traffic patterns highly affected the molecular distributions of PAHs, but did not significantly influence the overall PAH concentrations.

3.1.3. Effect of vehicle speed

Vehicle speed was also considered to be an affecting factor in the concentrations of air pollutants due to traffic exhaust. The total concentrations and molecular distributions of PAHs in road dust from roads having different vehicle speeds (low: 75 km/h, medium: 85 km/h, or high: 110 km/h) are shown in Fig. 5a–c.

The size characteristics of PAH concentrations in the road dust with different vehicle speeds have a similar pattern, as shown in Fig. 5a. The finest size of road dust particles also had the highest concentration of the total PAHs followed by the size of 75–180 μm. The higher PAH concentration in the particles of size 850–2000 μm in comparison to the size of 180–850 μm were due to the effects of new asphalt pavement. The ratios of the total PAH concentration for the particles of 850–2000 μm to those of 180–850 μm were 1.4, 4.1, and 6.0 in low, medium, and high-speed roads, respectively. The concentration ratio increased with increasing vehicle speed. The higher vehicle speed causes more friction, which is the main reason for road pavement abrasion.

The measured overall PAH concentration for medium-speed roads was the highest, followed by that of the low-speed road (Fig. 5b). In order to compare the true effect of vehicle speed on the PAH concentration within road dust, the difference in traffic volume among the roads with different speeds needed to be considered. The normalized overall PAH concentration, obtained by considering the traffic volume for each road speed, should be used for this comparison purpose. The low-speed road had the higher normalized concentration of PAHs in comparison to the medium-speed road. There were more emissions from vehicles per unit length of road on the low-speed road than in those on the medium-speed road. In order to pass through the same length of road on the low-speed road, vehicles might have spent a relatively increased amount of fuel and, therefore, would have emitted relatively more pollutants.

Fig. 5c shows the molecular distribution of the PAHs in road dust affected by different vehicle speeds. The fractions of the PAHs with 4-ring compounds were not much changed with vehicle speed of the roads. The correlation between vehicle speed and the relative concentration fractions of the total PAH concentration of the PAHs with 5- and 6-membered rings showed the opposite trend (Fig. 6). The concentration fractions of the PAHs with a 5-membered ring were inversely proportional to vehicle speed with a high coefficient of determination ($r^2 = 0.985$ with $p < 0.01$). However, the concentration fractions of the PAHs with a 6-membered ring proportionally increased, with vehicle speed having a very high correlation ($r^2 = 1.000$ with $p < 0.01$). The influence of traffic composition for each road speed on its molecular distribution of the PAHs was negligible because these roads had similar fractions of gasoline and diesel vehicles (76.6% and 81.2% of gasoline vehicles for the low and medium-speed roads, respectively).

3.1.4. Effect of surrounding area

There are many national scale industrial sites in Ulsan and, thus, the industrial emissions have a substantial affect on PAHs in road dust. A comparison of PAH concentration in the road dusts obtained from two kinds of residential areas, a typical urban residential area and a residential area near the industrial complex, are shown in Fig. 7a–c.

In comparison to the total PAH concentrations in different particle sizes, it is recognized that the finer particle sizes (i.e., less than 75 μm and 75–180 μm) were more affected by industrial activities than were the coarser particles (Fig. 7a). One more reason for the large increase in PAH concentration for smaller road dust particles near the industrial site area in comparison to the typical residential area would be its higher fraction of diesel vehicles, which produce more fine particles than do the gasoline vehicles. The gasoline and diesel vehicles fractions were 78.5% and 22.5% for the typical urban residential area, while 63.7% and 36.3% in the residential area near industrial sites, respectively.

Both measured and normalized overall PAH concentrations in road dust for the residential area near the industrial sites were much higher than those in the typical residential areas (Fig. 7b). This suggests that there is strong influence from industrial emissions on the PAH concentration found in road dust near industrial sites.

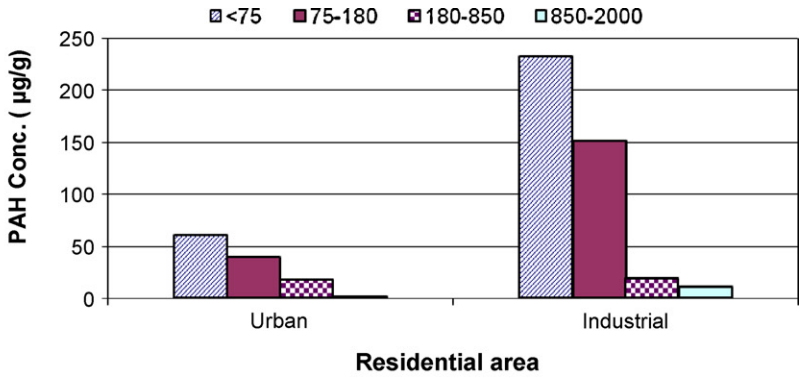
In the distribution studies of the aromatic ring number of the PAHs identified from engine emissions of vehicles [12,35], the emissions from gasoline engines included more PAHs with higher molecular weights, such as 5- and 6-membered ring PAHs, in comparison to diesel engine emissions. Thus, the greatly increased fraction of PAHs with a 5-membered ring in the typical urban residential area is due to an increase in emissions by a higher fraction of gasoline-powered vehicles in comparison to the residential area near the industrial site.

3.1.5. Traffic sources contribution to the PAH ratio

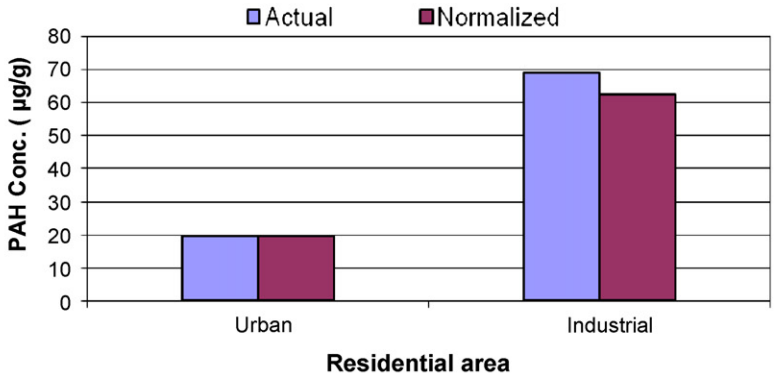
$\sum$COMB is a sum of FL, Pyr, BaA, CHR, BkF, BaP, BghiP, and IND concentrations, and it represents the typical combustion origin for PAH [36,37]. As the ratio of $\sum$COMB/$\sum$PAH increases, the fraction of the combustion origin PAHs increases. The ratio of $\sum$COMB/$\sum$PAH in road dust of Ulsan ranged from 0.73 to 0.93 with an average of 0.85, which represent higher fractions of the combustion origin PAHs. Fig. 8 shows bivariate plots of (a) PA/Ant versus FL/Pyr and (b) $\sum$COMB/$\sum$PAH versus FL/Pyr in road dust from Ulsan. The obtained values in the bivariate plots matched closely with the values identified from traffic areas recently reported by Wang et al. [37], except for two points and one point in Fig. 8a and b, respectively. This fact demonstrates that the road dust was greatly affected by traffic emissions.

3.2. Toxicity of PAHs in road dust

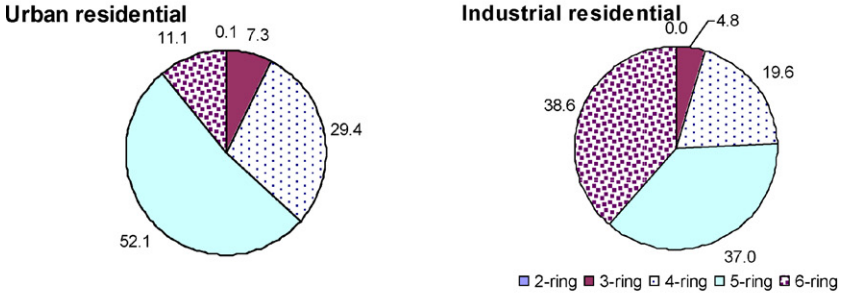
The toxic equivalency factors system proposed by Nisbet and LaGoy [30] was used to identify the toxicity of the PAHs identified in road dust from the study sites. The highest toxicity value of PAHs in road dust was obtained at a dense traffic rotary which also had the highest overall PAH concentration. There was a high correlation between the overall concentrations and the TEQs of



(a) size distribution of PAH concentration



(b) measured and normalized overall concentrations



(c) molecular distribution

Fig. 7. Concentrations of PAHs in road dust from different residential areas.

the PAHs within the road dust. The very high coefficient of determination ($r^2 = 0.955$ with $p < 0.01$) between them indicates that a higher total PAH concentration in road dust results in higher toxicity.

Even though the TEQs of the PAHs in road dust were proportional to the overall PAH concentrations, their correlations among different road dust particle sizes were different. The coefficient of determination between the total concentrations and the TEQs of the PAHs in the road dust size of 180–850 μm was an extremely high value, $r^2 = 0.998$ with $p < 0.01$. Their correlation in the road dust with a size of less than 75 μm was the lowest one ($r^2 = 0.514$ with $p < 0.01$) among the four size groups. A recent study that focused on the characteristics of PAHs found in road dust from industrial and urban areas in a typical industrial city determined that the coefficient of determination ($r^2 = 0.98$) between the TEQs and the total concentration of the PAHs in the road dust from the urban areas was much higher than that ($r^2 = 0.75$) of the industrial areas [28]. This difference in the degree of correlation was due to the complicated contribution from industrial and traffic emissions in road dust in industrial areas. The road dust from the residential area near the industrial site showed a substantial increase in the concentrations of PAHs in finer road dust than in coarser road dust, as discussed in the previous section. The finer road dust is substantially influenced by both traffic and industrial emissions that have different concentration profiles and toxicities of PAHs, in comparison to the coarse road dust, which has been greatly affected by suspended particulates released from fast moving vehicles [20]. Thus, a relatively lower correlation between the overall concentrations and the TEQ of the PAHs in finer road dusts represents a large contribution from industrial emissions.

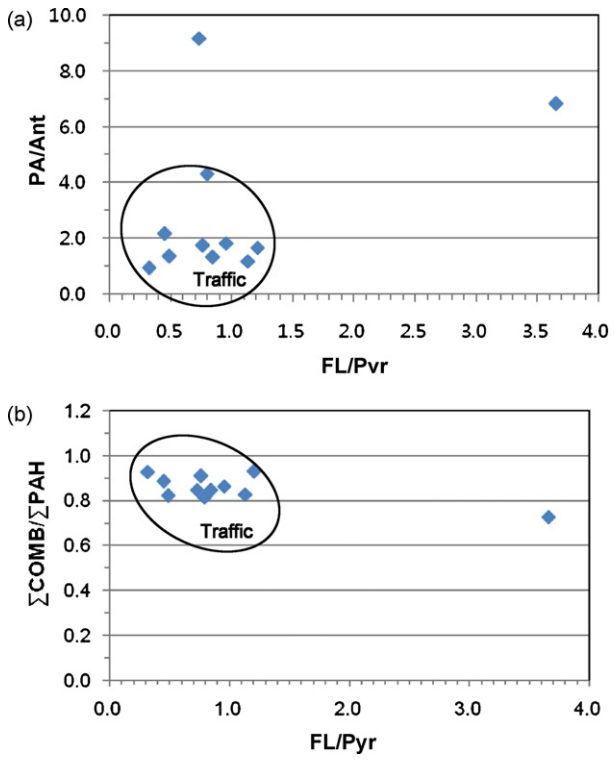


Fig. 8. Bivariate plots of (a) PA/Ant versus FL/Pyr and (b) $\sum$COMB/$\sum$PAH versus FL/Pyr.

4. Conclusions

The concentration of PAHs in road dust was greatly affected by road characteristics, such as pavement types, traffic volume, vehicle types, vehicle speed, and surrounding areas. This study reached the following conclusions:

1. Asphalt roads have a higher total PAH concentration for each particle size (except the size of 180–850 μm) in comparison to those of concrete roads. However, we found in one case that the overall PAH concentration in the road dust from one asphalt road was lower than that from a concrete road. This is because the overall PAH concentration is determined by the dominant particle size, in terms of weight, which was the size of 180–850 μm in both road types.
2. The traffic volume greatly affected the PAH concentration in road dust while the vehicle type strongly influenced the PAH molecular distribution. The road dust on roads with lower vehicle speeds showed higher concentrations of PAH than those particles collected from high-speed roads. However, higher vehicle speed caused greater pavement abrasion, resulting in increased concentrations of the PAHs, particularly for larger road dust particle sizes.
3. The concentrations of the PAHs in road dust from a residential area near an industrial site were much higher than those in a typical residential area.
4. The total PAH concentration for different particle sizes increased when the particle sizes decreased. This is because a group of smaller particles has a higher total available surface area for PAHs exposure. The coarsest particles, 850–2000 μm, resulting from abrasion of new asphalt pavement, had a higher total PAH concentration than those of size 180–850 μm.
5. The molecular distribution of PAHs varied greatly among different sites based on their traffic composition patterns and other local emissions.

The toxicities of PAHs in road dust have a strong linear relationship with the total PAH concentration ($r^2 = 0.955$). However, the correlation usually decreased with decreasing road dust particle size.

References

[1] B.A. Benner, G.E. Gordon, S.A. Wise, Mobile sources of atmospheric polycyclic aromatic hydrocarbon: a roadway tunnel study, Environ. Sci. Technol. 23 (1989) 1269–1277.
[2] Y. Chen, K.F. Ho, S.S.H. Ho, W.K. Ho, S.C. Lee, J.C. Yu, H.L. Sit, Gaseous and particulate polycyclic aromatic hydrocarbons (PAHs) emissions from commercial restaurant in Hong Kong, J. Environ. Monit. 12 (2007) 1402–1409.
[3] M.A. Hassanien, N.M. Abdel-Latif, Polycyclic aromatic hydrocarbons in road dust over Greater Cairo, Egypt, J. Hazard. Mater. 152 (2008) 247–254.
[4] R. Boonyatumanond, M. Murakami, G. Wayyatakorn, A. Togo, H. Takada, Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand, Sci. Total Environ. 384 (2007) 420–432.
[5] B.-K. Lee, C.B. Lee, Development of an improved dry and wet deposition collector and the atmospheric deposition of PAHs onto Ulsan Bay, Korea, Atmos. Environ. 38 (2004) 863–871.
[6] H.H. Yang, W.J. Lee, L.J. Theen, C.W. Kua, Particle size distribution and PAH content of road dust, J. Aerosol Sci. 28 (1997) S125–S126.
[7] H. Takada, T. Onda, N. Ogyra, Determination of polycyclic aromatic hydrocarbons in urban street dusts and their source materials by capillary gas chromatography, Environ. Sci. Technol. 24 (1990) 1179–1186.
[8] H. Takada, T. Onda, N. Ogyra, Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in street dust from the Tokyo Metropolitan Area, Sci. Total Environ. 107 (1991) 45–69.
[9] K.-P. Chang, G.-C. Fang, J.-C. Chen, Y.-S. Wu, Atmospheric polycyclic aromatic hydrocarbons (PAHs) in Asia: a review from 1999 to 2004, Environ. Pollut. 142 (2006) 388–396.
[10] G.-C. Fang, Y.-S. Wu, J.-C. Chen, P.P.-C. Fu, C.-N. Chang, T.-T. Ho, M.-H. Chen, Characteristic study of polycyclic aromatic hydrocarbons for fine and coarse particulates at Pastureland near Industrial Park sampling site of central Taiwan, Chemosphere 60 (2005) 427–433.
[11] G.-C. Fang, C.-N. Chang, Y.-S. Wu, P.P.-C. Fu, I.-L. Yang, M.-H. Chen, Characterization, identification of ambient air and road dust polycyclic aromatic hydrocarbons in central Taiwan, Taichung, Sci. Total Environ. 327 (2004) 135–146.
[12] L.C. Marr, T.W. Kirchstetter, R.A. Harley, A.H. Miguel, S.V. Hering, S.K. Hammond, Characterization of polycyclic aromatic hydrocarbons in motor vehicles fuel and exhaust emissions, Environ. Sci. Technol. 33 (1999) 3091–3099.
[13] A.M. Mastral, M.S. Callén, R. Murillo, T. Garcia, Combustion of high calorific value waste material: organic atmospheric pollution, Environ. Sci. Technol. 33 (1999) 4155–4158.
[14] M. Liu, S.B. Cheng, D.N. Ou, L.J. Hou, L. Gao, L.L. Wanf, Y.S. Xie, Y. Yang, S.Y. Xu, Characterization, identification of road dust PAHs in central Shanghai areas, China, Atmos. Environ. 41 (2007) 8785–8795.
[15] R.K. Aryal, H. Furumai, F. Nakajima, M. Boller, Characteristics of particle-associated PAHs in a first flush of a highway runoff, Water Sci. Technol. 53 (2006) 245–251.
[16] M. Murakami, F. Nakajima, H. Furumai, Size- and density-distributions and sources of polycyclic aromatic hydrocarbons in urban road dust, Chemosphere 61 (2005) 783–791.
[17] R. Boonyatumanond, G. Wattayakorn, A. Togo, H. Takada, Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand, Mar. Pollut. Bull. 52 (2006) 942–956.
[18] S. Dahle, V.M. Sanivov, G.G. Matishov, A. Evenset, K. Næs, Polycyclic aromatic hydrocarbons (PAHs) in bottom sediments of the Kara Sea shelf, Gulf of Ob and Yenisei Bay, Sci. Total Environ. 306 (2003) 57–71.
[19] E.J. Hoffmann, J.S. Latimer, C.D. Hunt, G.L. Mills, J.G. Quinn, Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters, Environ. Sci. Technol. 18 (1984) 580–587.
[20] E. Manoli, A. Kouras, C. Samara, Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbon from three sites in northern Greece, Chemosphere 56 (2004) 867–878.
[21] M. Murakami, F. Nakajima, H. Furumai, Modelling of runoff behaviour of particle-bound polycyclic aromatic hydrocarbons (PAHs) from roads and roofs, Water Res. 38 (2004) 4475–4483.
[22] J.D. Butler, V.W. Butter, C. Kellow, H.G. Robinson, Some observations on the polycyclic aromatic hydrocarbons (PAH) content of surface soils in urban areas, Sci. Total Environ. 38 (1984) 75–85.
[23] J.D. Li, X.D. Zhang, S.H. Li, G.Q. Qi, X.Z. Liu, Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, GuangZhou, South China, Sci. Total Environ. 355 (2006) 145–155.
[24] L.-B. Liu, Y. Liu, J.-M. Lin, N. Tang, K. Hayakawa, T. Maeda, development of analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulate: a review, J. Environ. Sci. 19 (2007) 1–11.
[25] M.E. Aydin, S. Ozcan, A. Tor, Ultrasonic solvent extraction of persistent organic pollutants from airborne particles, Clean 35 (2007) 660–668.
[26] X.H. Bi, G.Y. Sheng, P.A. Peng, Y.J. Chen, Z.Q. Zhang, J.M. Fu, Extractable organic matter in PM_{10} from LiWan district of Guangzhou city, PR China, Sci. Total Environ. 300 (2002) 213–228.

[27] Z. Guo, T. Lin, G. Zhang, L. Hu, M. Zheng, Occurrence and sources of polycyclic aromatic hydrocarbons and *n*-alkanes in $PM_{2.5}$ in the roadside environment of a major city in China, J. Hazard. Mater. 30 (2009) 888–894.
[28] T.T. Dong, B.-K. Lee, Characteristics, toxicity, and source apportionment of polycyclicaromatic hydrocarbons (PAHs) in road dust, Chemosphere 74 (2009) 1245–1254.
[29] IARC (International Agency for Research on Cancer), Complete List of Agents Evaluated and their Classification, http://monographs.iarc.fr/ENG/Classification/index.php.
[30] C. Nisbet, P. LaGoy, Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs), Reg. Toxicol. Pharmacol. 16 (1992) 290–300.
[31] M. Pufulete, J. Battershill, A. Boobis, R. Fielder, Approaches to carcinogenic risk assessment for polycyclic aromatic hydrocarbons: a UK perspective, Reg. Toxicol. Pharmacol. 40 (2004) 54–66.
[32] T. Petry, P. Schmid, C. Schlatter, The use of toxic equivalency factors in assessing occupational and environmental health risk associated with exposure to airborne mixtures of polycyclic aromatic hydrocarbons (PAHs), Chemosphere 32 (1996) 639–648.
[33] M. Tavares Jr., J.P. Pinto, A.L. Souza, I.S. Scarminio, M.C. Solci, Emission of polycyclic aromatic hydrocarbons from diesel engine in a bus station, Londrina, Brazil, Atmos. Environ. 38 (2004) 5039–5044.
[34] W. Rogge, L.M. Hiddlemann, M.A. Mazurek, G.R. Cass, B.R.T. Simonelt, Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks, Environ. Sci. Technol. 27 (1993) 636–651.
[35] S.M. Corrêa, G. Arbilla, Aromatic hydrocarbons emissions in diesel and biodiesel exhaust, Atmos. Environ. 40 (2006) 6821–6826.
[36] H.M. Hwang, T.L. Wade, J.L. Sericano, Concentrations and source characterization of polyaromatic hydrocarbons in pine needles from Korea, Mexico, and United States, Atmos. Environ. 37 (2003) 2259–2267.
[37] Z. Wang, J. Chen, X. Qiao, P. Yang, F. Tian, L. Huang, Distribution and sources of polycyclic aromatic hydrocarbons from urban to rural soils: a case study in Dalian, China, Chemosphere 68 (2007) 965–971.