Concentration, distribution and gas/particle partitioning of atmospheric PAHs in rural, urban and industrial sites of northern Taiwan

Nguyen-Duy Dat, Moo-Been Chang
Graduate Institute of Environmental Engineering, National Central University (NCU), Zhongli, 320, Taiwan

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds composed of multiple aromatic rings which are ubiquitous and well-recognized as carcinogenic, teratogenic and genotoxic compounds [1]. Therefore, investigating the occurrence of atmospheric PAHs is important for reducing human exposure to these toxic pollutants. Significant anthropogenic sources of PAHs include stationary combustion sources and mobile sources. The most important sources of atmospheric PAHs are incomplete combustion processes, pyrolysis of materials containing carbon and hydrogen, such as coal, oil, wood and petroleum products [2]. Taoyuan City, a highly industrialized and densely populated city located in northern Taiwan, has the high potential risk of PAHs. Investigating the concentrations, distributions, sources and gas/particle partitioning of atmospheric PAHs collected in different sites would provide the information for better understanding the PAH characteristics in this area. In order to investigate the characteristics of PAHs in different areas located in Taoyuan City, ambient air samples were simultaneously collected from 3 sites, including a rural site (roof top of a 4-story building located in NCU campus), an urban site (roof top of a 5-story building in a high school campus located in Zhongli District) and an industrial site (roof top of a 2-story office in an industrial park).

Materials and methods

Two samples were collected at each site in winter (20-24th February,2017) using Sibata high-volume air samplers at a sampling rate of 500 L min^{-1}, each sample was collected in 2 days with the total volume of 1400 m^3. Gas-phase PAHs were adsorbed by a sandwich cartridge of PUF/XAD-2/PUF containing 30 g XAD-2 and a TE-1123-4 PUF, while particulate-phase PAHs were collected by quartz fiber filter (QFF). Samples were extracted and cleaned up according to the California Air Resources Board (CARB) Method 429 and 16 priority PAHs were analyzed by GCMS using a fused silica capillary column DB-5 MS (60 m × 0.25 mm × 0.25 m) under positive EI condition, and all data were obtained in the selected ion monitoring (SIM) mode.

Results and discussion

Average gas- and particulate-phase PAH concentrations at three sampling sites are presented in Table 1. The highest PAH concentration is found at the urban site (225.1 ng m^{-3}), followed by industrial site (157.2 ng m^{-3}) and rural site (147.8 ng m^{-3}). The PAHs levels obtained in this study are comparable with the PAHs concentrations measured in an industrial park (Kaoshiung, Taiwan) [3], but lower than the levels reported in China [4]. Gas-phase PAHs strongly dominates in atmosphere, accounting for 98.85, 98.55, and 98.35 % of total PAHs in urban, rural and industrial sites, respectively. In general, low molecular weight (LMW) PAHs are abundant congeners in gas phase and heavy PAHs are dominated in particulate phase. NAP and PHE are dominant species in gas phase of three sites, however, dominant PAHs are different in particle phase of different sites, for instance, IcdP (17.3%), BbF (15.4%) and BghiP (14.6%) are dominated in urban site, NAP (20%), BbF (12.6%) and BkF (11.7%) are abundant in rural site, while FLT (15%), Bghi, PHE, BbF, PYR and ANT (10-10.8%) dominate in industrial site. Although total PAH concentration measured in industrial site is significantly lower than that measured in urban site and is comparable with that measured in rural site, the total concentration of 7 PAHs (from ACY to PYR) measured in industrial site are significantly higher than that of two other sites. The results suggest that the major source contributes to PAHs in industrial site is different from two other sites.

Table 1: Average concentration of atmospheric PAHs in three sites (ng m^{-3})

	Urban site		Rural site		Industrial site	
	Gas-phase	Particulate-phase	Gas-phase	Particulate-phase	Gas-phase	Particulate-phase
NAP	197.9	0.065	125.4	0.431	107.7	0.070
ACY	1.512	0.004	1.014	0.007	2.031	0.012
ACE	0.815	0.001	0.620	0.001	0.751	N.D
FLU	4.005	0.007	2.793	0.011	5.322	0.005
PHE	10.48	0.111	9.092	0.106	24.03	0.278
ANT	0.688	0.008	0.617	0.004	2.583	0.260
FLT	3.965	0.259	3.089	0.221	6.135	0.393
PYR	2.752	0.186	2.709	0.134	5.700	0.269
BaA	0.122	0.113	0.141	0.058	0.098	0.104
CHR	0.220	0.164	0.238	0.119	0.175	0.160
BbF	0.014	0.399	0.008	0.270	0.011	0.270
BkF	0.005	0.134	0.007	0.251	0.009	0.100
BaP	N.D.	0.281	N.D.	0.097	0.014	0.131
DahA	N.D.	0.029	N.D.	0.020	N.D.	0.017
IcdP	N.D.	0.449	N.D.	0.189	0.008	0.280
BghiP	N.D.	0.379	N.D.	0.229	0.007	0.239
Total (ng m^{-3})	222.5	2.590	145.7	2.149	154.6	2.588
(ng BaP-TEQ m^{-3})	0.245	0.418	0.169	0.201	0.207	0.227

N.D.: non-detected

The average ambient temperatures of sampling sites are in the range of 14.2-19.4 ^{o}C during sampling period. TSP concentrations range from 35.10 to 119.9 µg m^{-3}, with the highest concentration being measured in industrial site, followed by urban site and rural site and a negative correlation between TSP and rainfall was observed for all sites. However, significant correlation between particle-phase PAHs and rainfall was only found in urban site. Furthermore, in urban and industrial sites, gas-phase PAH concentrations decrease as the rainfall increases and temperature decreases. Several studies indicate that temperature is an important parameter affecting atmospheric PAHs concentration with a negative correlation [5,6]. This result indicates that rainfall is more important than temperature in affecting PAHs concentration.

Being similar to mass concentration, the highest BaP TEQ concentration was found at urban site (0.663 ng BaP-TEQ m^{-3}), followed by industrial site (0.434 ng BaP-TEQ m^{-3}) and rural site (0.370 ng BaP-TEQ m^{-3}). Generally, contribution of particulate-phase PAHs to BaP-TEQ concentration is higher than that of gas-phase PAHs due to the higher association of heavy PAHs which are of higher TFF values and predominate in particulate phase. NAP is the major contributor to gas-phase BaP-TEQ concentration (52-80%), while BaP is the main contributor to particle-phase BaP-TEQ concentration (49-66%).

Diagnostic ratios were used effectively as indicators of PAH sources by various studies [7]. In this study, the diagnostic ratios of FLU/(FLU+PYR), ANT/(ANT+PHE), BaA/(BaA+CHR) and IcdP/(IcdP+BghiP) were employed to identify possible PAH sources of the samples collected. As presented in Table 2, several important sources might contribute to PAHs at each site. Briefly, urban site may be affected by diesel emission, petrogenic source, vehicular emission and combustion, while industrial site might be influenced by petrol emission, pyrogenic source and combustion. Rural site PAHs are contributed by various sources including petrol, diesel emission, petrogenic source, combustion and vehicular emission.

Table 2: Comparison between diagnostic ratios obtained in this study and references.

PAH ratio	UB01	UB02	RR01	RR02	ID01	ID02	Value range and corresponding sources (summarized by [7])
FLU/(FLU+PYR)	0.574	0.581	0.520	0.479	0.490	0.431	<0.5: Petrol emissions >0.5: Diesel emissions
ANT/(ANT+ PHE)	0.059	0.065	0.042	0.077	0.104	0.105	<0.1: Petrogenic >0.1: Pyrogenic
BaA/(BaA+ CHR)	0.340	0.422	0.251	0.410	0.365	0.388	<0.2: Petrogenic 0.2-0.35: Coal combustion >0.35: Vehicular emissions, or combustion
IcdP/(IcdP + BghiP)	0.541	0.547	0.545	0.351	0.523	0.551	<0.2: Petrogenic, 0.2-0.5: Petroleum combustion >0.5: Grass, wood and coal combustion

UB: Urban site, RR: rural site, ID: industrial site

Gas-particle partitioning of PAHs was evaluated by logK_p value. K_p is the gas-particle partitioning coefficient (m^3 μg^{-1}) which can be calculated following Pankow (1987) [8]. Results show that logK_p increases from -4.86 to -0.68 as the ring number of PAHs increases from 2 to 5, which indicates that heavier PAHs have higher tendency to associate with particle phase. This result is consistent with the observation reported by Wang et al. (2011) [4]. Furthermore, in order to understand possible mechanisms governing the gas/particle partitioning of PAHs, logK_p-logP^0_L relationship is also evaluated as presented in Figure 1. LogP^0_L, a temperature-dependent value, is log of the PAH sub-cooled liquid vapor pressure which can be calculated by equations established by Odabasi et al. (2006) [9]. Two important mechanisms govern the gas/particle partitioning of PAHs in ambient air, including physical adsorption onto the aerosol surface and absorption into the aerosol organic matter. Both mechanisms lead to a linear relationship between logK_p and the log of the PAH subcooled liquid vapor pressure (logP^0_L) [4]. Ideally, under equilibrium conditions, the slope mr should be equal to -1 if either adsorption or absorption mechanism explain gas/particle PAH partitioning. While slope significantly steeper than -1 indicates adsorption on a rather strong adsorbent and slope shallower than -0.6 suggests absorption into an absorbent with high cohesive energy. Slopes in the range of -0.6 to -1 occur when either absorption or adsorption may be the mechanism [10]. As shown in Figure 1, correlations between logK_p and logP^0_L (R^2 = 0.938-0.955) are significant in all three sites. The mr values of rural and urban sites (-0.877, -0.876, respectively) are closer to -1 than that of industrial site (-0.758), indicating that gas/particle partitionings of PAHs collected in rural and urban sites are closer to equilibrium state than that of industrial site. Moreover, the sorption and desorption of newly released PAHs to aerosols may take hours to reach equilibrium during transportation [11], therefore, the result also indicates that PAHs collected in industrial site may be more related to local emission compared with two other sites. On the other hand, the slopes obtained are in the range of -0.6 to -1, indicating that both absorption and adsorption are possible mechanisms for gas/particle partitioning of PAHs in the samples collected.

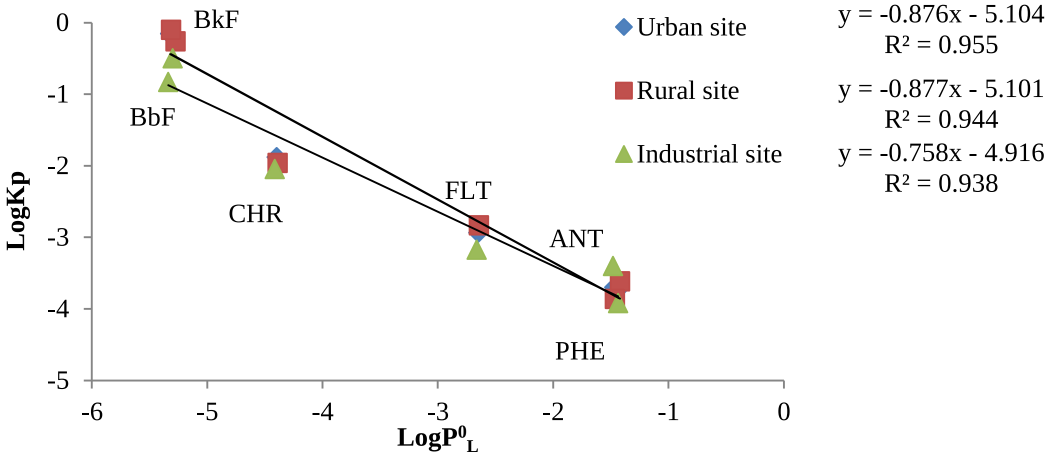

Figure 1: LogKp-logP^0_L relationship based on calculated logKp, log P^0_L of PHE, ANT, FLT, CHR, BbF, BkF

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