*Vietnam Journal of Science and Technology **55** (4C) (2017) 97-102*

GAS–PARTICLE PARTITIONING OF POLYCYCLIC AROMATIC HYDROCARBONS - PAHs IN AMBIENT AIR IN HOCHIMINH CITY

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Received: …; Accepted for publication: 19 October 2017

ABSTRACT

This research conducted an analysis of 14 Polycyclic Aromatic Hydrocarbons (PAHs) in gas and particle-phase in ambient air in Hochiminh City to investigate their occurence and the gas/particle distribution. Gas and particle samples were collected from June to August 2015 in Hochiminh City and PAHs were treated and analyzed using high performance liquid chromatography with fluorescence detection (HPLC/FLD). Results showed that average concentration of 14 PAHs were from 6.4 to 29.8 ng/m^3 and from 50.7 to 133 ng/m^3 in particle-phase and in gas-phase, respectively. The concentration of PAHs in the gas-phase accounted for more than 80% of total PAHs concentration in which low molecular weight PAHs as the dominant PAHs. Meanwhile, high molecular weight PAHs distributed mainly in particle-phase. The particle-phase fraction Φ was obtained to understand the partitioning.

*Keywords***:** Polycyclic Aromatic Hydrocarbons (PAHs), gas/particle partitioning, High Performance Liquid Chromatography (HPLC), Hochiminh City.

1. INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are widely distributed to environmental pollutants. They are products of the incomplete combustion of organic matter. Anthropogenic emission sources of PAHs in the atmosphere include traffic, domestic heating, oil refining and other industrial processes [1, 2]. PAHs are ubiquitous constituents of urban airborne particulates and are of major health concern mainly due to their well-known carcinogenic and mutagenic properties. PAHs occur in both gas and particle-phase in the atmosphere, depending on the volatility of the PAH species. Most high molecular weight PAHs which are higher carcinogenic and mutagenic are in particle-phase[3, 4, 5].

Gas/particle partitioning can be quantified by gas/particle partition coefficient, K_p ($m^3\mu g^{-1}$). K_p can be obtained from experiment and using the equation $(C_p/C_{TSP})/C_g$ where C_p and C_g are particle and gas-phase concentration of PAHs (ng/m^3) and C_{TSP} is TSP concentration in the air [2]. In recent year, the particle–phase fraction Φ - $C_p/(C_p+C_g)$ has been received more attention [3].

Hochiminh City is the largest industrial and commercial center in the south of Vietnam, with a population of about 8.2 million people. The study of PAHs has received little attention because of expensive and complex analytical method and, consequently, very little information is available for PAHs in the atmosphere in Hochiminh City, especially gas/particle partitioning of PAHs. Studies conducted by Hien et al. [1, 6] provide initial information about PAHs in Hochiminh City. Therefore, this study aimed to investigate the concentration and gas/particle distribution of 14 PAHs in ambient air in order to provide helpful information for further environmental policy of these harmful compounds in Hochiminh City.

2. MATERIALS AND METHODS

2.1. Sampling

The map of sampling sites was illustrated in Figure 1. The sites D2, D3, D5, D10 and Binhtan are located in the center of the city while Binhchanh and Thuduc are suburban sites and near industrial area. Samples were collected by using a high volume sampler Sibata 500R at a flow rate of 300 L/min in 22 hours. Particle-phase PAHs were collected on glass fiber filters while gas-phase PAHs were adsorbed in 3 pieces of polyurethane foams PUFs. Samples were monthly collected at 8 sampling sites in Hochiminh City in the rainy season from June to August 2015.

2.2. Sampling preparation

Glass filters were wrapped in aluminum foil, heated for 8hours at 400^{o}C and stored in desiccator at least 2 days. By weighting the filter before and after sampling the particle mass of samples can be determined. PUFs were extracted in soxhlet system with diethyl ether 5% in hexane for 16 hours then wrapped in aluminum foil. PUFs were taken to the field in glass jar capped with teflon lids.

2.3. PAHs analysis

All chemical solvents used in this study were of chromatographic grade. Certified PAHs standard solution (EPA 610 PAHs) were from Supelco/Sigma-Aldrich**,** USA. 14 PAHs were determined including: acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthrancene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[ah]anthracene (DahA), benzo[ghi]perylene (BghiP) and indeno[1,2,3-cd]pyrene (InP).

The particle-phase PAHs extraction and determination were followed by Hien et al. in 2007 [1, 6]. Particle-phase PAHs were ultrasonic extracted with benzene:ethanol 3:1 for 20 minutes. The extracts were filtered and cleaned with NaOH, H_2SO_4 and mili Q water, respectively. Then, dehydration via anhydrous sodiumsulfate column. The extracts were concentrated by rotary

evaporator and almost dryness under a stream of pure nitrogen, PAHs were dissolved in 1mL of MeOH and stored at -4^{o}C until analysis by HPLC with fluorescence detector.

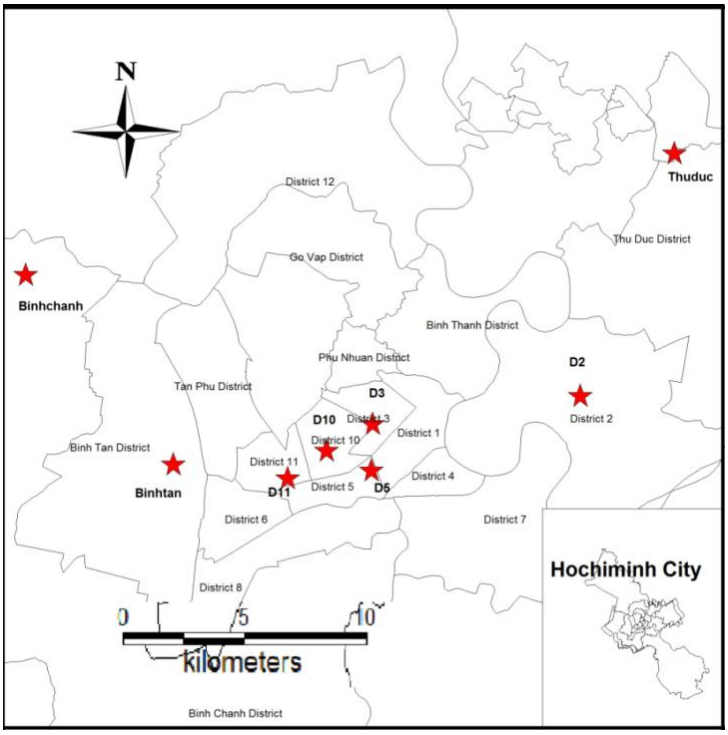

Figure 1. Map of the sampling sites in Hochiminh City.

For gas-phase PAHs, Compendium Method TO-13A, USEPA was used. Sample PUFs were soxhlet extracted with diethyl ether 5% in hexane for 16 hours, then the extract was concentrated by rotary evaporator and evaporated to near dryness under a stream of pure nitrogen, PAHs were dissolved in 1mL of MeOH and stored at -4^{o}C until analysis by HPLC with fluorescence detector. All measurements were carried out using a HPLC-FLD (Shimadzu including LC – 20AD pump, CTO – 20A column oven, SIL – 20A auto sampler, Inersil ODS – P 5 µm (4.0 × 250 mm) column). The recovery test was performed by spiking known amounts of a mixture of PAHs onto the filter and then the spiked filter was treated by the same way as field samples. The average recovery of each PAH was calculated from 6 replicated measurements of the spiked samples. The average recoveries for PAHs were 81-144% with the relative standard deviations of 7-49%. Method detection limit MDL and method quantitation limit MQL were measured based on blank sample with spike of PAHs standard. MDL of the PAHs compounds in particle-phasevaried from 0.1 pg/m^3 for Ant and BkF to 20 pg/m^3 for Ace. While in the gas-phase, MDL varied from 0.2 pg/m^{3}for BaP to 2.95 pg/m^3 for Phe.

3. RESULT AND DISCUSSION

3.1. PAHs concentration at the sampling sites

The total PAHs concentration in particle and gas-phase was shown in Table 1. Total PAHs in particle-phase ranged from 6.4 to 29.8 ng/m^3, with an average of 14 ± 7 ng/m^3. The total

PAHs at suburban sites Binhchanh and Thuduc were clearly larger than those of D2, D5, D10 at urban sites. The concentration of total PAHs was the highest at Binhchanh (29.8 ng/m^3) and BaP concentration at this site was 4.6 ng/m^3. Industrial activity near suburban sites significantly contributed to PAHs concentration in both particle and gas-phase in these sites. The European Commission has recommended a limit value between 0.5 and 1.0 ng/m^3 for BaP [7]. The average concentration of BaP at all sampling sites (excepted D5) exceeded the European standard that implied high health risk for human in the area. BghiP was the dominant PAH in particle-phase in Hochiminh City.

Table 1. Total 14 PAHs concentration in gas and particle-phase.

Sampling sites	Particle-phase PAHs Mean± SD ng/m^3	Gas-phase PAHs Mean ± SD ng/m^3
D2	10.206 ± 2.290	59.810 ± 3.048
D3	15.959 ± 6.187	91.941 ± 20.006
D5	6.450 ± 0.114	57.413 ± 13.152
D10	9.540 ± 2.356	50.724 ± 25.154
D11	13.628 ± 1.197	102.256 ± 28.111
Binhchanh	29.822 ± 5.554	87.266 ± 62.086
Binhtan	12.832 ± 1.045	133.202 ± 51.434
Thuduc	13.990 ± 12.267	80.656 ± 31.301
HCMC	14.054 ± 7.040	82.908 ± 27.331

As shown in Table 1, the total PAHs concentration in gas-phase was much higher than those in particle-phase, varied from 50.7 to 133 ng/m^3 with an average of 82.9 ± 27.3 ng/m^3. The total PAHs concentration in gas-phase accounted for 85.5±5 % of total PAHs in the air which was similar to the study of Masao et al. in Hanoi [8]. Phe was the highest PAH in gas-phase at all sampling sites ranged from 25 to 63.9 ng/m^3, average of 41 ± 13 ng/m^3, and accounted for approximately 50% of gas-phase PAHs. Ace had the lowest concentration in both gas and particle-phase.

Measured PAHs were categorized into 3 groups. Low molecular weight LMW-PAHs (2, 3 rings) are Ace, Flu, Phe and Ant. Middle molecular weight MMW-PAHs (4 rings) are Flt, Pyr, BaA and Chr. High molecular weight HMW-PAHs (5, 6 rings) are BbF, BkF, BaP, DahA, BghiP and InP. Figure 2 and 3 showed the PAHs fraction in particle and gas-phase. HWM-PAHs such as BaP, DahA, Bghi, InP with more toxic than the other PAHs were found mainly in particle-phase (63.81%). In contrast, LMW and MMW-PAHs were approximately 99.9% of total PAHs concentration in gas-phase. These PAHs have less toxic than HMW-PAHs, however Ace, Flu, Ant, Pyrcan react with $^{\bullet}OH$ and $NO_3^{\bullet}$ radicals in the gas phase to form nitro-PAHs. Some nitro-PAHs are higher mutagenicity (2-105 times) and carcinogenicity (10 times) in human being's cells than their parent PAHs [9]. The percent of molecular weight PAHs between gas and particle-phase were shown in Figure 4, more than 80% of LMW-PAHs and HMW-PAHs in the ambient air were in the gas-phase, and 95% of HMW-PAHs in the ambient air were in the particle-phase. This is due to difference of vapor pressure of PAHs.

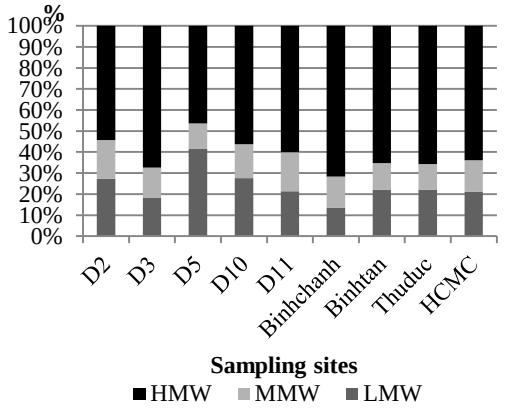

Figure 2. PAHs fraction in particle-phase.

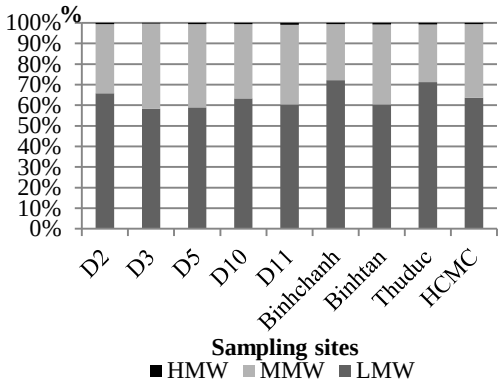

Figure 3. PAHs fraction in gas-phase.

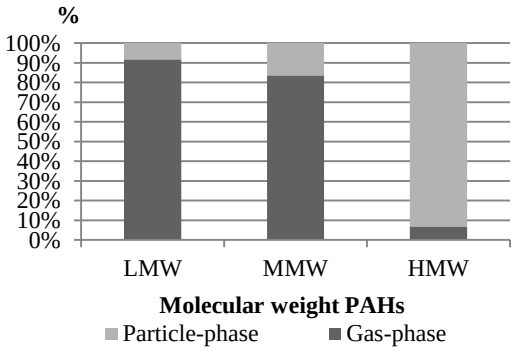

Figure 4. Molecular weight PAHs in gas and particle-phase.

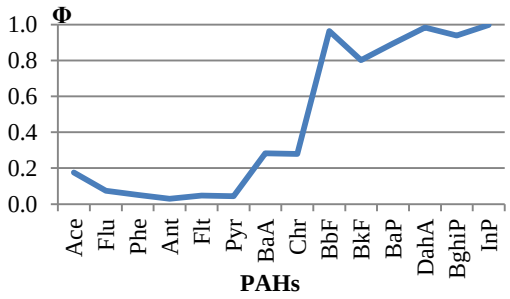

Figure 5. The particle–phase fraction Φ.

3.2. Gas/particle partitioning of PAHs

The gas/particle partitioning of PAHs is based on the particle characteristics (size distribution, chemical composition, and carbon content), vapor pressure and atmospheric conditions (temperature, relative humidity) [3]. In our study, the particle–phase fraction Φ ($C_p/(C_p+C_g)$) was used for assessing the gas/particle partitioning of PAHs.The particle-phase fraction Φ was shown in Figure 5. The Φ of 3,4 ring-PAHs (from Ace to Chr) were lower than 0.5 therefore they mainly distributed in gas-phase while the Φ of 5, 6 ring-PAHs (BbF, BkF, BaP, DahA, BghiP and InP) were larger than 0.5 and reached to the ratio of 1. In Osaka, Φ valueswere found smaller than 0.5 for Flu, Phe, Ant, Flt, Pyr, larger than 0.5 for BaA and reached to 1 for BkF, BaP, BghiP, InP [4]. The difference could be explained by the different temperature between Osaka, Japan and Hochiminh City. In Osaka, the average temperature of sampling period was 16.2^{o}C cooler than in Hochiminh City (28.9^{o}C), therefore vapor pressures of PAHs were smaller. The very clear difference was obtained for BaA whose Φ values were 0.9 in Osaka and 0.3 in Hochiminh City, respectively.

4. CONCLUSION

PAHs were determined in gas and particle-phase from June and August 2015 in Hochiminh City. PAHs concentrations in particle-phase were higher at the suburban sites compared to the

urban sites. PAHs were dominant in gas-phase with more than 80%. The Φ of 3, 4 ring-PAHs were lower than 0.5 therefore they mainly distributed in gas-phase while the Φ of 5, 6 ring-PAHs were larger than 0.5 and were the highest PAHs in particle-phase. From the value of Φ, we can estimate the concentration of PAHs in the gas phase from the data of PAHs in the particle phase.

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