

CHARACTERISTICS OF AMBIENT PAHS COLLECTED IN HO CHI MINH CITY, VIETNAM

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Introduction

Ho Chi Minh City (HCMC) is the most densely populated city and has the highest traffic density in Vietnam which is facing serious air pollution problem. Vehicles and industrial activities in HCMC may potentially emit PAHs. Investigation of PAH characteristics including level, potential source and health assessment is necessary. In this study, ambient air samples were collected using high volume air samplers at five sites (UTE, UOS, BT, PN and NB) during dry season (from March to May 2018) and two sites (UTE and UOS) during rainy season (from August to October 2018). Three samples were collected at each site and 25 PAHs in gas and particulate phases were analyzed using GC/MS following isotope dilution method.

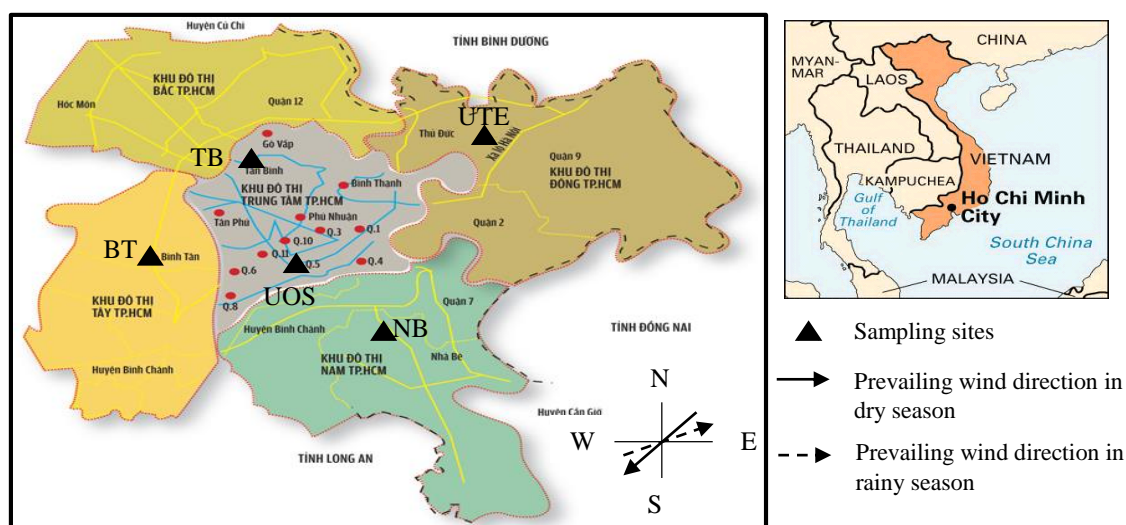


Fig 1: Locations of sampling sites

Materials and methods

Samples were collected using high-volume air samplers PS1 at a sampling rate of 250 L/min. Each sample was collected for 2 days with the total volume of 600 m³. Gas-phase PAHs were adsorbed by a sandwich cartridge of PUF/XAD-2/PUF containing 15 g XAD-2 and a PUF (Tisch Environmental), while particulate-phase PAHs were collected by quartz fiber filter (QFF, Advantec, Japan). Prior to sampling, XAD-2 and PUF were pre-cleaned in Soxhlet extractor with toluene for 24 hrs and were dried by a nitrogen gas stream at 50°C in a vacuum oven to remove toluene, while the filters were baked at 500°C for 4 hrs to remove any traces of organics and weighed at

ambient temperature. Fluorene-D10 and p-Terphenyl-D14 are added into the sandwich cartridges as surrogate standards before sampling. After sampling, QFF and sandwich cartridge were individually wrapped in aluminum foil and stored at $<5^{\circ}\text{C}$ until analysis.

Procedures of pretreatment and analysis of PAHs were clearly presented in previous publication¹. Briefly, samples were extracted for 24 hours by Soxhlet extraction with dichloromethane (DCM). All samples were added an isotope-spiked solution of PAHs (Wellington Laboratories Inc.) before extraction to quantify the concentration of each PAH congener. The DCM extract was then concentrated and cleaned up using activated silica gel column. The collected eluent was reconcentrated to approximately 200 μL , with a gentle nitrogen stream and was added recovery standards before analysis. Twenty-five PAHs including 15+1 EU-PAHs, 16 US-PAHs, benzo[e]pyrene (BeP) and Perylene (PER) were analyzed by GCMS (Agilent 6890-5973N) using a fused silica capillary column DB-5 MS (60 m \times 0.25 mm \times 0.25 μm) under positive EI conditions, and data were obtained in the selected ion monitoring (SIM) mode. Naphthalene is excluded due to the contamination level in cartridges.

Results and discussion

Mass and TEQ concentration of PAHs measured in this study are presented in Fig. 1. Results indicate that higher mass PAH concentrations are measured in rainy season compared with those in dry season. The PAH concentration measured in dry season ranges from 8.79 to 33.2 ng/m^3 (average: $22.2 \pm 5.93 \text{ ng}/\text{m}^3$), while that measured in rainy season ranges from 26.0 to 60 ng/m^3 (average: $43.6 \pm 11.8 \text{ ng}/\text{m}^3$). While BaP-TEQ concentration measured in dry season ranges from 4.05 to 12.6 $\text{ng BaP-TEQ}/\text{m}^3$ ($8.39 \pm 2.48 \text{ ng BaP-TEQ}/\text{m}^3$), and that measured in rainy season ranges from 3.85 to 12.2 $\text{ng BaP-TEQ}/\text{m}^3$ ($8.01 \pm 2.63 \text{ ng BaP-TEQ}/\text{m}^3$), which are significantly higher than the level of 1 $\text{ng BaP-TEQ}/\text{m}^3$ as regulated by many countries².

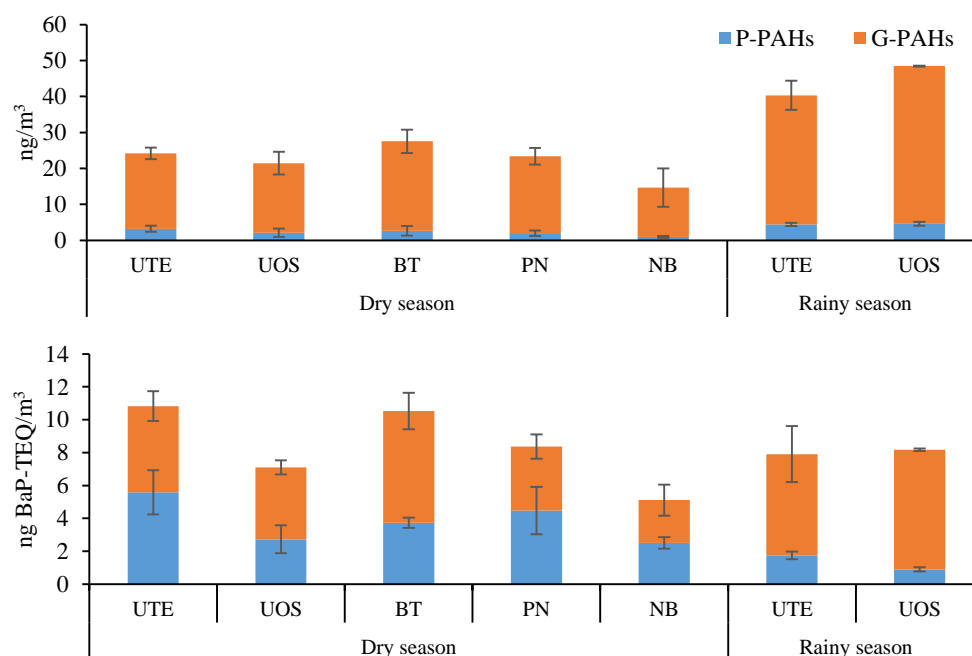


Fig. 2 Mass (a) and BaP-TEQ (b) concentrations of PAHs measured in this study

As presented in Fig. 2, gaseous PAHs mainly contribute to total mass concentration, ranging from 84 to 95% ($91 \pm 3\%$), while gaseous PAHs contribute to 36-72% of total TEQ concentration. Higher contribution of

particulate PAHs to TEQ concentration is due to higher association of high ring PAHs which are of higher TEF values in particulate phase compared with that in gas phase as presented in Fig. 3. In terms of mass concentration, 3- and 4-ring PAHs are major contributors to gaseous PAHs, accounting for 96-99%, while 5- and 6-ring PAHs are main contributors to particulate PAHs, accounting for 73-90%. Phenanthrene (PA) is the major contributor to gaseous PAHs (34.5-47.5%), followed by Fluorene (Flu, 10.5-28%), Floranthene (FL, 9.2-19.0%) and Pyrene (Pyr, 8.3-18.2%), while Ideno[123-cd]pyrene (I1,2,3-cd) is a major contributor to particulate PAHs (12.7-29.2%), followed by Benzo[ghi]perylene (Bg,h,iP, 9.9-26.1%) and Benzo(b)fluoranthene (BbF, 7.3-16.2%). In terms of BaP-TEQ concentration, Dibenzo[a]lpyrene (Da,1A, 80-96%) and Benzo[c]fluorene (BcFE, 96-99%) are the main contributors to particulate and gas phases, respectively in the dry season. In rainy season, BcFE is the main contributor to BaP-TEQ in gaseous PAHs, however, Da,1A (34-44%), BcFE (19-32%) and BaP (16-28%) are major contributors to particulate PAHs measured in UTE, while Benzo(a)pyrene (BaP, 26-18%), BcFE (24-28%) and Da,hA (9-10%) are the main contributors to particulate PAHs collected at UOS. All of these congeners are of high TEF values, such as $TEF_{BcFE} = 20$, $TEF_{Da,1A} = 30$, $TEF_{BaP} = TEF_{Da,hA} = 1$.

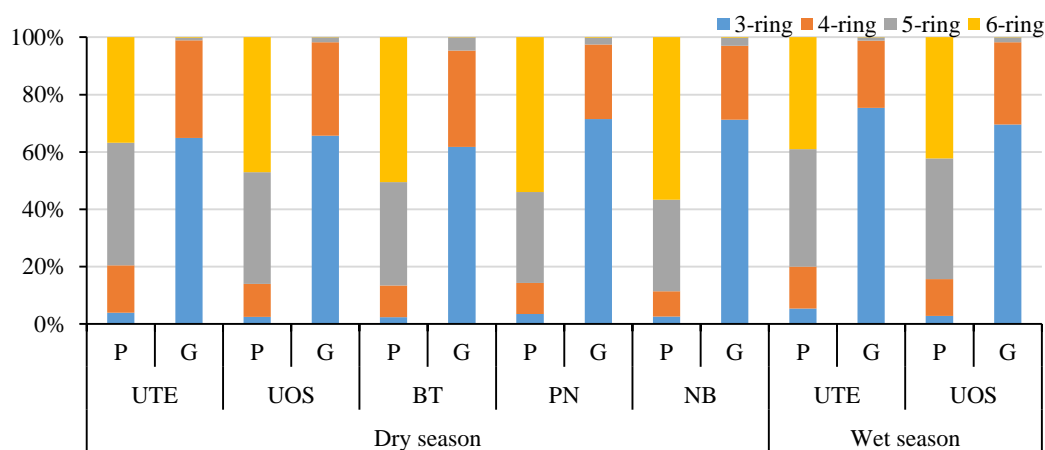


Fig. 3 Distribution of PAHs in gas and particulate phases

The contributions of 15+1 EU-PAHs and 15 US EPA-PAHs to total BaP-TEQ concentration are presented in Table 1. Obviously, 15+1 EU-PAHs can present total TEQ concentration of 25 PAHs analyzed in both gas and particulate phases, while 15 US EPA PAHs under-estimate the total TEQ concentration of 25 PAHs analyzed. The results indicate that 16 US EPA PAHs are inadequate to address the toxicity of PAHs in ambient air collected in HCMC.

Table 1. Contributions of 15+1 EU PAHs and 16 US EPA PAHs to total TEQ concentration

	Dry season		Rainy season	
	Particle	Gas	Particle	Gas
15+1 EU PAHs	99.9±0.04%	99.5±0.11%	99.6±0.14%	99.3±0.14%
15 US EPA PAHs	5.81±2.7%	1.79±0.59%	42.5±13%	2.09±0.15%

Diagnostic ratios are applied effectively as indicators of PAH sources by various studies¹. In this study, the diagnostic ratios including BaA/(BaA+ CHR) and IcdP/(IcdP+BghiP) are employed to figure out potential sources of PAHs collected in HCMC. $IcdP/(IcdP+BghiP) < 0.2$ indicates petrogenic source, $IcdP/(IcdP+BghiP) = 0.2-0.5$ is

petroleum combustion and $IcdP/(IcdP+BghiP) > 0.5$ indicates grass, wood and coal combustion³. $BaA/(BaA+CHR) < 0.2$ indicates petroleum evaporation, $BaA/(BaA+CHR) = 0.2-0.35$ is from coal combustion and $BaA/(BaA+CHR) > 0.35$ is related to vehicular emission or combustion^{3,4}. As presented in Fig. 3, vehicular emission, and combustion of grass, wood, coal and petroleum are the main sources of PAHs collected. The ratio of $IcdP/(IcdP+BghiP)$ divides samples to two groups and indicates that PAHs collected in dry season are more related to combustion of grass, wood and coal, while PAHs collected in rainy season are more related to petroleum combustion.

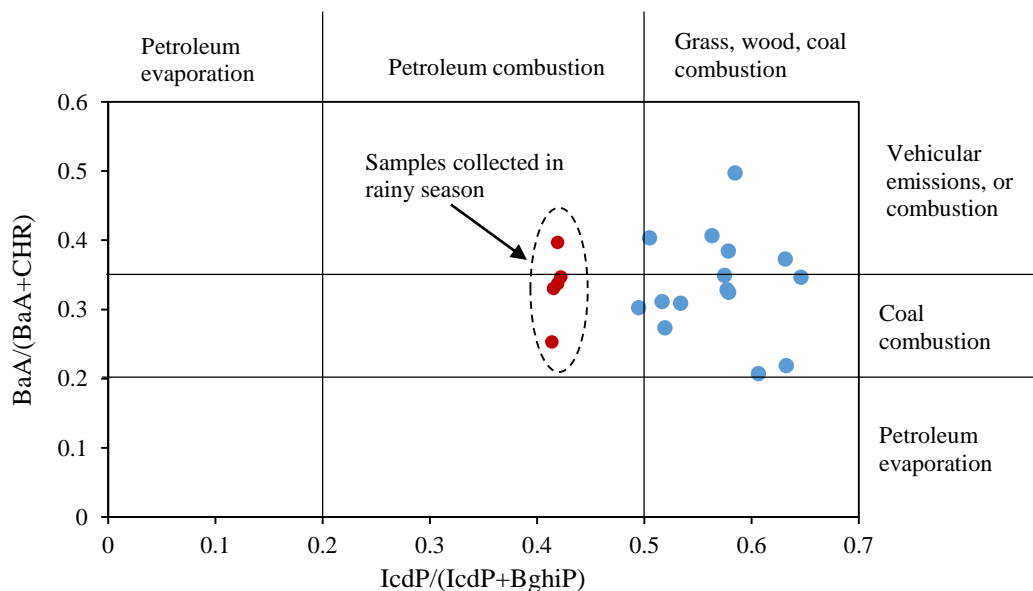


Fig. 3 Diagnostic ratios of $BaA/(BaA+CHR)$ and $IcdP/(IcdP+BghiP)$

Conclusions

Higher concentration of PAHs is measured in rainy season compared with that in dry season. The BaP-TEQ concentration of PAHs measured in HCMC is significantly higher than the level of 1 ng/m^3 regulated in many countries (up to 10 times higher), indicating severe PAHs pollution in HCMC. Diagnostic ratios indicate that PAH sources are related to vehicular emission, and combustion of grass, wood, coal and petroleum might contribute to PAHs measured in HCMC as well.

Acknowledgements

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