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A comparison of $PM_{2.5}$ and PAHs in ambient air between an urban background site and a background site in Ho Chi Minh city

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Abstract:

This study aims to evaluate the differences between $PM_{2.5}$, PAHs concentration, PAHs species, and their gas/particle partitioning in an urban background site as opposed to another background site. Saigon zoo was selected as a representative of the urban background site (UBS), and the Can Gio mangrove reserve was selected as the other background site (BS). $PM_{2.5}$ and gas and particle-phase PAHs samples were collected at the UBS between March 2017 and February 2018, while the samples were collected at the BS for one week in the dry season (April) and in the rainy season (October). The results demonstrated that both $PM_{2.5}$ and PAHs concentrations at the UBS were significantly higher than those at the BS. The $PM_{2.5}$ concentration at the UBS and BS ranged from 13.3 to 67.6 µg/m^3 and from 5.1 to 22.7 µg/m^3, respectively. The total concentration of 14 PAHs at the UBS was 2.6 times greater than that at BS. Phenanthrene (Phe) was the dominant PAH in ambient air at both sites. Benzo[g,h,i]perylene (BghiP) and Indeno[1, 2, 3-cd]pyrene (InP), which indicate the traffic source, accounted for 3.6 and 3.3% of total PAHs at the UBS, while that at the BS accounted for 1.5 and 1.3%, respectively. This result suggested that vehicular emission strongly affected the UBS site.

Keywords: **Can Gio mangrove, gas/particle partitioning, $PM_{2.5}$, polycyclic aromatic hydrocarbons (PAHs), Saigon zoo.**

Classification number: **5.2**

Introduction

Particulate matter (PM) is a critical measure of atmospheric pollution due to its effect onthe environment. Particles are defined by their aerodynamic diameters; for example, $PM_{2.5}$ has aerodynamic diameters of less than 2.5 µm. $PM_{2.5}$ causes detrimental health effects because when they are inhaled, they can penetrate deep into the alveoli of the lungs and become deposited there. The size of $PM_{2.5}$ particulate matter is not the only notable factor for health effects; the chemical composition is also important [1]. Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion of organic matter, and they are ubiquitous in our environment. Anthropogenic emission sources of PAHs in the atmosphere include traffic, domestic heating, oil refining, and other industrial processes [2, 3]. PAHs are well-known because of their carcinogenic and mutagenic properties. PAHs associated with fine particles, which can deeply infiltrate the human respiratory system, may cause severe problems to human health. Research regarding air quality of background sites has provided information concerning the contributions of local sources, whether they are from regional backgrounds or from long-range transport [4]. In Ho Chi Minh city, studies of background air quality are limited. This study aims to evaluate the differences in $PM_{2.5,}$ PAHs concentration, PAHs species, and their gas/particle partitioning between UBS and BS. Fourteen PAHs analysed in both gas and particle phases included 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[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP), and indeno[1,2,3-cd]pyrene (InP).

Materials and methods

Sampling

Saigon zoo in Ho Chi Minh city (10.787°N,106.707°E) was selected as are presentative for the UBS because it is not

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heavily influenced by either traffic or industrial emissions. Can Gio (10.615°N,106.816°E), located in southeastern Ho Chi Minh city, was selected as the BS of the city. The distance between the two sampling sites is about 20 kilometers. A map of the sampling sites is illustrated in Fig. 1. $PM_{2.5}$, and gas and particle-phase PAH samples were collected at the UBS between March 2017 and February 2018, while the samples were collected at the BS for one week in the dry season (April) and in the rainy season (October). $PM_{2.5}$ was collected on quartz fiber filters, and an impactor was used at a flow rate of 10 l/min in 24 hours [5]. A high-volume sampler was used to collect gas phase and particle phase PAHs simultaneously running at a flow rate of 200 l/min in 24 hours. Particle-phase PAHs were collected on glass fiber filters, and gas-phase PAHs were adsorbed on polyurethane foams (PUFs) [6]. The samplers were set up at 1.5 meters above the ground. A total of 90 $PM_{2.5}$ samples and 24 gas and particle-phase PAHs samples and 14 $PM_{2.5}$ samples and 14 gas and particle-phase PAHs samples were collected at the UBS and BS, respectively.

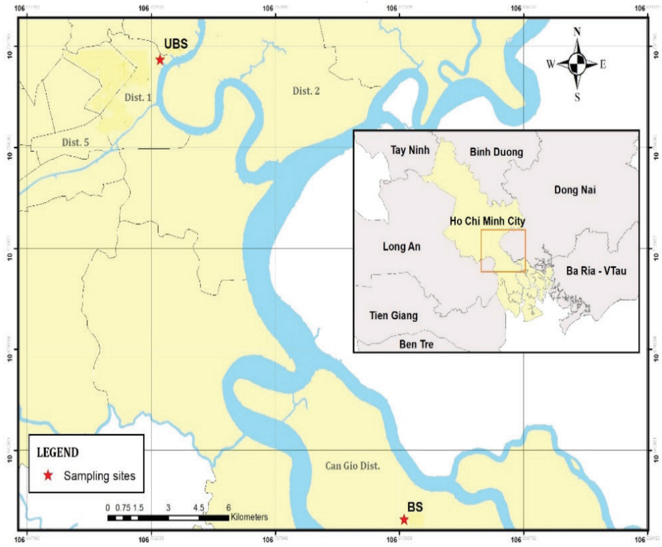

Fig. 1. Map of the sampling sites.

Sampling preparation

Glass and quartz filters were wrapped in aluminum foil, heated for 8 hours at 400^0C, and placed in a desiccator at least 2 days. The particle mass of samples was determined by weighing the filters before and after sampling using a RADWAG6 Digit Micro Balance. PUFs were extracted from as oxhlet system with 5% diethyl ether in hexane left for 16 hours; they were then wrapped in aluminum foil. The PUFs were brought to the sampling sites in glass jars sealed with teflon lids.

Chemical analysis

Particle-phase PAHs were extracted through sonication three times in the toluene and ethanol (3/1, v/v) solvent; the solution was then filtered to remove solid substances. The filtrate was cleaned up with NaOH, followed by H_2SO_4 and Millipore water. The extract was concentrated by a rotary evaporator and was evaporated to near dryness using a gentle stream of nitrogen. The residue was completely dissolved in methanol. The extract was stored after passing through a 0.45 μm syringe filter until it was injected into the High-Performance Liquid Chromatography with Fluorescence Detection (HPLC-FLD) system for analysis [7].

Compendium Method TO-13A, USEPA was used for gas phase PAHs [6]. PAHs in PUFs were extracted from a soxhlet system with 5% diethyl ether in hexane left for 16 hours. The extract was concentrated further by a rotary evaporator to near dryness under a stream of pure nitrogen. The PAHs were then dissolved in methano land stored at -4^0C until analysis by a HPLC-FLD machine.

All measurements were performed using a Shimadzu HPLC-FLD machine (including an LC - 20AD pump, a CTO - 20A column oven, a SIL - 20A auto sampler, and aInersil ODS - P 5 μm (4.0 × 250 mm) column). The recovery test was determined by spiking known amounts of a mixture of PAHs standards on to a filter or PUF; the spiked sample was then treated in the same manner as the field samples. Six measurements of the spiked samples were replicated for calculating the recovery of PAHs. The recovery results for particle-phase PAHs were 57.6-104.8%, with the relative standard deviations of 2.4-15.4%; for gas-phase PAHs, they were 95.2-182.5%, with the relative standard deviations of 5.42-56.6%. The method detection limit (MDL) of the PAH compounds in particle-phase varied 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 [8]. Laboratory blanks and field blanks for correcting the potential contamination from the experiment were prepared and analysed as samples. Microsoft Excel was used for statistical analysis.

Results and discussion

Atmospheric concentration of $PM_{2.5}$

$PM_{2.5}$ samples were collected at the UBS between March 2017 and February 2018, while the samples were collected at the BS for one week in the dry season (April) and in the rainy season (October). A summary of average concentrations of $PM_{2.5}$ at the BS and UBS during the sampling period is illustrated in Fig. 2. The $PM_{2.5}$ concentration at the UBS was significantly higher than level at the BS. The $PM_{2.5}$ concentration ranged from 13.3 to 67.6 μg/m^3, with a mean of 35.4±12.9 μg/m^3 and from 5.1 to 22.7 μg/m^3 with a mean of 13±5.8 μg/m^3 at the UBS and BS, respectively. The $PM_{2.5}$ concentration at UBS in the dry season was higher than in the rainy season (t-test, $p<0.05$), while there was no difference at the BS. Relative to other background sites in the world, the

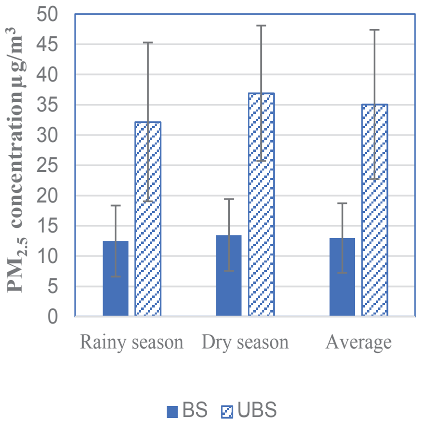

Fig. 2. Summary of $PM_{2.5}$ concentration at the BS and UBS during the sampling period.

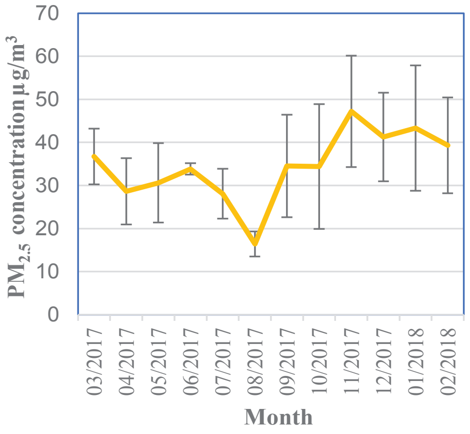

Fig. 3. Monthly average concentration of $PM_{2.5}$ at the UBS from 3/2017 to 2/2018.

$PM_{2.5}$ concentration at the UBS was significantly higher than at an urban background in Southeastern Italy 5.5-31.6 µg/m^3 [4] and a rural background area in Spain 12-17 µg/m^3 [9].

Figure 3 indicated the monthly average concentration of $PM_{2.5}$ at the UBS between March 2017 and February 2018. The $PM_{2.5}$ concentration tended to decrease in the rainy season and increase in the dry season. Wet deposit was pivotal in removing particles in the rainy season. There were 10 days (which accounted for 11% of entire data) when the $PM_{2.5}$ concentration at UBS exceeded the Vietnam National Technical Regulation on Ambient Air Quality QCVN 05:2013/BTNMT. The annual $PM_{2.5}$ concentration of 35.1±5.8 µg/m^3 also exceeded the regulation, demonstrating a high risk of long-term exposure to human health.

This study has found that the $PM_{2.5}$ concentration was exceptionally high on the 18th of January 2018, with the value of 67.6 µg/m^3 higher than the others in this month. However, the $PM_{2.5}$ concentration at Ho Chi Minh city US Consulate air monitoring station was also high, with a value of 69.3 µg/m^3. To understand this event, the Hypslit model provided by NOAA was used. The backward trajectory result on the 18th of January 2018 is illustrated in Fig. 4. The result of a 72-hour trajectory demonstrates that the air mass came from the East-North-East direction, from the Philippines to Ho Chi Minh city. At 6 pm on the 15th of January 2018, the height of air mass was about 2500 m, which was the same as the Mayon volcano that erupted on this day. It was clear that the $PM_{2.5}$ from the Mayon volcanic eruption was transported to Ho Chi Minh city. Based on this result, it is important to recognize this special event and investigate how it affects air quality and human health.

Atmospheric concentration of PAHs

Table 1 displays a summary of average concentrations of 14 PAHs as well as the total PAH concentrations measured in gas and particle-phases during the sampling period.

Total PAH concentration in the particle-phase varied from 1.4 to 9.1 ng/m^3 (with an annual mean of 4.28 ng/m^3) and from 0.3 to 1.6 ng/m^3 (with an annual mean of 0.84 ng/m^3) at the UBS and BS, respectively. There was also a seasonal trend; the particle-phase PAHs were higher in the rainy season, while the gas-phase PAHs were higher in the dry season at the UBS. $PM_{2.5}$-bound PAHs accounted for 91.8% of total PAHs in the particle-phase, particularly high molecular weight PAHs such as BaP, BghiP, and InP. This result is similar to the study of Céline Liaud [10]. Significant correlations were obtained for the following PAHs (DahA, BbF, BkF, BghiP, InP) in the $PM_{2.5}$, indicating that these high-molecular weight PAHs and $PM_{2.5}$ presented common pollution sources. Gas-phase PAHs ranged from 13.4 to 47.7 ng/m^3 (with an annual mean of 29.46 ng/m^3) and from 5.7 to 20.7 ng/m^3 (with an annual mean of 11.91 ng/m^3) at the UBS and BS, respectively. The gas-phase PAHs at both sites were larger than those in the particle-phase and tended to increase in the dry season when the temperature rose. Phe was the dominant PAH at both sampling sites. BghiP and InP which indicates traffic source accounted for 3.6 and 3.3% of total PAHs at the UBS, while those at the BS accounted for 1.5 and 1.3%, respectively. This result suggested that vehicular emission heavily affected the UBS site. Indeed, Sai Gon zoo (UBS) is located in the center

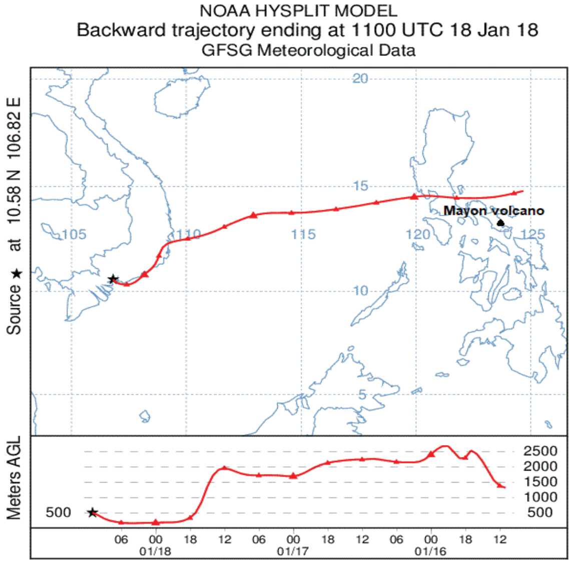

Fig. 4. 72-hour air trajectory ending on the 18th of January 2018 at the UBS (backward trajectory result using Hysplit model).

Table 1. Summary of annual and seasonal mean concentrations of 14 PAHs and the total PAH concentrations (ng/m^3) measured in gas-phase and particle-phases at the UBS and BS during the sampling period.

Sampling sites	UBS			BS		
PAHs ng/m^3	*Average* *(Gas and particle phase)*	*Rainy season* *(Gas and particle phase)*	*Dry season* *(Gas and particle phase)*	*Average* *(Gas and particle phase)*	*Rainy season* *(Gas and particle phase)*	*Dry season* *(Gas and particle phase)*
Ace	0.04/0.01	0.06/0.01	0.02/BDL	0.01/BDL	BDL/BDL	0.04/BDL
Flu	3.02/0.05	2.65/0.07	3.47/0.02	1.19/0.03	1.12/0.02	1.34/0.07
Phe	16.84/0.29	15.90/0.39	17.99/0.17	6.56/0.16	5.01/0.07	10.18/0.35
Ant	1.06/0.02	1.11/0.02	0.99/0.01	0.38/0.01	0.20/BDL	0.79/0.02
Flt	3.95/0.17	3.69/0.18	4.27/0.16	1.84/0.06	1.55/0.05	2.52/0.09
Pyr	3.87/0.18	3.74/0.18	4.03/0.17	1.59/0.05	1.35/0.04	2.13/0.06
BaA	0.15/0.08	0.12/0.08	0.19/0.07	0.06/0.02	0.04/0.01	0.10/0.02
Chr	0.27/0.14	0.21/0.14	0.35/0.13	0.12/0.03	0.10/0.03	0.18/0.05
BbF	0.01 /0.03	0.01/0.03	0.02/0.03	0.01/0.01	0.01/0.01	BDL/BDL
BkF	0.09/0.23	0.09/0.26	0.09/0.20	0.06/0.03	0.06/0.03	0.05/0.02
BaP	0.09 /0.38	0.12/0.39	0.05/0.36	0.03/0.05	0.02/0.05	0.04/0.06
DahA	0.01/0.29	0.02/0.33	BDL/0.26	BDL/0.08	BDL/0.08	BDL/0.06
BghiP	0.04/1.24	0.04/1.43	0.04/0.10	0.06/0.15	0.06/0.16	0.07/0.13
InP	0.01/1.17	0.02/1.41	BDL/0.88	BDL/0.17	BDL/0.17	BDL/0.19
Total	**29.46/4.28**	**27.78/4.94**	**31.51/3.47**	**11.91/0.84**	**9.53/0.71**	**17.45/1.12**

BDL: below detection limit.

of Ho Chi Minh city and surrounded by streets with high traffic density. There are few sources emitting PM$_{2.5}$ and PAHs at Can Gio (BS); additionally, those sources are stable throughout the year. This is why PM$_{2.5}$ and particle-phase PAHs were low, with a non-seasonal trend.

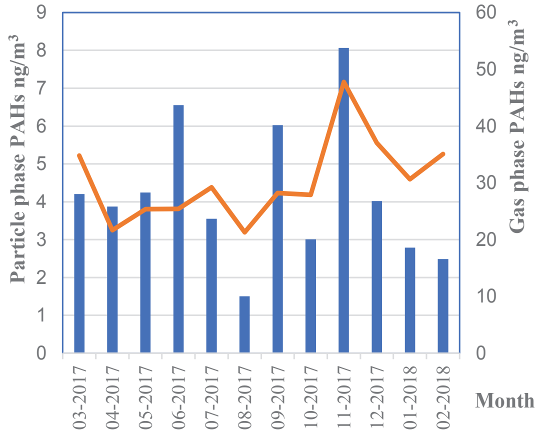

Fig. 5. Monthly mean concentration of gas-particle phase PAHs at the UBS during sampling period.

Monthly concentrations of total PAHs in gas and particle-phases at the UBS are illustrated in Fig. 5. Total PAHs had the lowest value in August and had the highest value in both gas and particle-phases in November. PAHs are well-known because of their carcinogenic and mutagenic potency for humans. BaP is a representative PAH because it is one of the most potent carcinogens known. The health risk assessment of PAHs can be determined based on its BaP equivalent concentration (BaP$_{eq}$). For each PAH, BaP$_{eq}$ is calculated by multiplying its concentration with the corresponding toxic equivalent factor (TEF). The European Commission has recommended a limit value for BaP of 1 ng/m^3 (Table 2).

Table 2. The BaPeq concentration (ng/m^3) at the UBS and BS.

BaP$_{eq}$	**Gas-phase Average±SD (Min-Max)**	**Particle-phase Average±SD (Min-Max)**
UBS	0.14±0.045 (0.058-0.24)	0.77±0.47 (0.18-1.89)
BS	0.055±0.034 (0.014-0.14)	0.15±0.098 (0.029-0.30)

The average BaP$_{eq}$ at UBS was 0.91 ng/m^3. In three months (September, November and December), the BaP$_{eq}$ concentration were 1.3, 2 and 1.1 ng/m^3 exceeding the European Commission. The BaP$_{eq}$ in the particle-phase accounted for 84%; notably, high-molecular weight PAHs, which is the strongest toxicity PAHs, displayed a dominant concentration. The average BaP_{eq} at the BS was 0.2 ng/m^3, which was 4.5 times lower than at the UBS.

Gas/particle partitioning of PAHs

High-molecular weight PAHs were dominant and accounted for 77.5% of the particle-phase PAHs. In contrast, low-molecular weight PAHs were also dominant and accounted for 71.2% of the gas-phase PAHs. Ace was below the detection limit in both phases, because Ace is easily decomposed by photochemical reaction in atmosphere. The particle-phase fraction Φ - $C_p/(C_p+C_g)$ was calculated to understand the PAHs' gas/particle partitioning, where C_p is the concentration of particle-phase PAH, and C_g is the concentration of gas-phase PAH (Table 3).

Table 3. The particle-phase fraction Φ of individual PAHs at the UBS and BS.

	Flu	Phe	Ant	Flt	Chr	BbF	BkF	BaP	DahA	BghiP
UBS	0.017	0.018	0.016	0.049	0.329	0.846	0.686	0.829	1.000	0.963
BS	0.027	0.021	0.009	0.033	0.199	0.565	0.242	0.779	1.000	0.750

The Φ of three-and four-ringPAHs at both sites were similar. The Φ of three-and four-ring PAHs (from Flu to Chr) were lower than 0.5, indicating that these PAHs are primarily distributed during the gas-phase. The Φ of five- and six-ringPAHs (BbF, BaP, DahA, BghiP) were larger than 0.5 and close to 1, which indicated that these PAHs are dominant in the particle-phase. However, there is a different Φ of BkF between the UBS and the BS. The Φ value at the BS was below 0.5, which did not align with other previous studies [3, 8]. Therefore, further research should be conducted to understand this situation.

Conclusions

This study has aimed to compare the $PM_{2.5}$, PAHs concentrations at two background sites and to provide more information about regional air quality in Ho Chi Minh city. The $PM_{2.5}$ and PAH concentrations at the UBS were substantially higher than those at the BS. The $PM_{2.5}$ concentration decreased in the rainy season and increased in the dry season. The Mayon volcanic eruption affected Ho Chi Minh city's atmosphere. Further evaluation is necessary to understand the effects of this event on human health. The BaP_{eq} in September, November, and December of 2017 exceeded the European Commission for PAHs, indicating a high risk of exposure. This study suggests that when investigating urban air pollution, it is necessary to assess not only the urban background but also the regional background, which will provide more information to understand local and long-range transport sources.

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The authors declare that there is no conflict of interest regarding the publication of this article.

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