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Atmospheric polycyclic aromatic hydrocarbons in air samples of Hanoi

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ABSTRACT

A survey on sixty five components of polycyclic aromatic hydrocarbons (PAHs) contained in particulate matter (PM) and in gas phase was conducted in Hanoi. Particulate and gaseous PAHs were collected on the quartz fiber filter (QFF) and on the polyurethane foam (PUF) plugs, respectively. Averages of particulate and gaseous total 65 PAHs concentrations (Σ 65PAHs) were 63 ± 82 and 1200 ± 480 ng m⁻³, respectively. The highest values of the particulate and gaseous ones at a location of No.9 were 290 and 2000 ng m⁻³, respectively. The values of gaseous PAHs were approximately 20 times higher than those of particulate ones. The PAHs were mainly originated from pyrogenic sources of gasolines engines. The ratio of the specific components contained in the particulate PAHs suggested that the automobile engines without catalytic converter were popular in Vietnam.

KEYWORDS

gaseous PAHs, Hanoi, particulate PAHs, polyurethane foam (PUF), quartz fiber filter (QFF)

INTRODUCTION

Since 1986, the economy of Vietnam has been rapidly growing up due to Doi Moi policy that was an introduction of a free market economy system into a socialistic country. The country has been industrialized, and the numbers of motorcycles have been drastically increased in the urban areas. As a result, it is apprehensive for the air pollutions (Hien et al., 2005; Lan et al., 2004) such as suspended particulate matters (SPM), nitrogen oxide (NO_x), sulfur oxide (SO_x), volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs) in urban cities.

Pollutions of PAHs in the environment have been of great concern, since some of PAHs have been reported to be mutagenic and/or carcinogenic for human health (Waller, 1952). Especially, most of 4- to 6- aromatic rings of PAHs, benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), chrysene, benz[*a*]anthracene (BaA) that exist in the particulate matter (PM) in the atmosphere are considered to be carcinogenic and/or mutagenic (Commins, 1962; Lao et al., 1973). Many surveys have been conducted on the particulate PAHs collected on the filters to evaluate their distribution and toxicity. On the contrary, the low molecular weight PAHs such as naphthalene and phenanthrene are reported to be mainly distributed into gas phase (Yamasaki et al., 1982), and they would react with other pollutants such as ozone and/or NO_x to form more toxic compounds (Park et al., 2001)

In this report, particulate and gaseous PAHs in air samples were investigated at ten locations of Hanoi, Vietnam. From the evaluation of the components in the PAHs, we estimated the origin of the emission sources of the particulate and gaseous PAHs.

MATERIALS AND METHODS

PAHs investigated were classified into six categories depending on the number of aromatic rings in the molecule as follow;

- 2 ring : naphthalene, benzo[*b*]thiophene, 1-,2-methylnaphthalene, biphenyl, 2,6-, 2,7-, 1,3-, 1,4-, 2,3-, 1,5-, 1,2-dimethylnaphthalene, and 2,3,5-trimethylnaphthalene.
- 3 ring : acenaphthylene, biphenylene, acenaphthene, fluorene, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, dibenzothiophene, phenanthrene, anthracene, 1-,2-phenylnaphthalene, *o*-, *m*-, *p*-terphenyl, 1-,2-, 3-, 4-, 9-methylphenanthrene, 2-,9-methylanthracene, 3,6-dimethylphenanthrene, and 9,10-dimethylanthracene.
- 4 ring : 1,2,3,4-tetrahydrofluoranthene, 4H-cyclopenta[*def*]phenanthrene (4H-CdefP), pyrene, fluoranthene, benzo[*b*]fluorene (BbF), 1,1-binaphthyl, 9-phenylanthracene, benz[*a*]anthracene (BaA), triphenylene, chrysene, naphthacene, and 7-methylbenz[*a*]anthracene (7-MeBaA).
- 5 ring : benzo[*b*]fluoranthene (BbF), benzo[*j*]fluoranthene (BjF), benzo[*k*]fluoranthene (BkF), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), perylene, 3-methylcholanthrene, 7-methylbenzo[*a*]pyrene (7-MeBaP), 9,10-diphenylanthracene, and 1,2,3,4-, 1,2,5,6-dibenzanthracene.
- 6 ring : indeno[1,2,3-*cd*]pyrene (INcdP), benzo[*ghi*]perylene (BghiP), anthanthrene, naphtho[2,3-*a*]pyrene, and 3,4,8,9-dibenzopyrene.
- 7 ring : coronene.

The urban air samples were collected at ten locations of Hanoi as shown in Table 1. Sampling of air samples were carried out by using minipumps (SHIBATA, MP-Σ500) at a flow rate of 5 l/min for 24 hrs. The air sample was passed through the quartz fiber filter (QFF) ($\phi=32$ mm) for the collection of the particulate PAHs and then through the two pieces of polyurethane foam (PUF) plug ($\phi=22$ mm, height=76 mm) for the gaseous ones. The particulate PAHs was defined as the PAHs collected on a QFF, whereas gaseous PAHs was defined as those collected with the two pieces of PUF plugs.

Table 1 Sampling locations and date in Hanoi

Site No.	Site description in Hanoi	Sampling date
1	Cau Moi Bridge	05 to 06/Aug./2005
2	De La Thanh and Nguyen Chi Thanh	09 to 10/Aug./2005
3	Lieu Gai Street, near intersection of Hoang Hoa Tham and Lieu Giai	10 to 11/Aug./2005
4	Ton Duc Thang and Kham Thien	11/Aug./2005
5	Dai Co Viet and Giai Phong	15 to 16/Aug./2005
6	Tran Nhan Tong and Ba Trieu	16/Aug./2005
7	Tran Hung Dao and Le Duan	27 to 28/Aug./2005
8	Le Hong Phong and Dien Bien Phu	28 to 29/Aug./2005
9	Long Bien intersection	29 to 30/Aug./2005
10	Hanoi Opera House	30 to 31/Aug./2005

After sampling, 10 ng of six surrogate standards (naphthalene-*d*₈, phenanthrene-*d*₁₀, chrysene-*d*₁₀, BaP-*d*₁₂, benzo[*ghi*]perylene-*d*₁₂, and coronene-*d*₁₂) were added onto QFF and PUF. The QFFs and the PUFs were separately extracted with dichloromethane (DCM) by using Soxhlet apparatus for 24 hrs and by ultrasonic extraction for 10 min (3 times repeated), respectively. The extracts were

concentrated and then dissolved into hexane. The concentrates were cleaned up with 5 g of 5% hydrous silica gel column chromatograph. The first fraction was eluted with 10 ml of hexane, and then the second fraction with 80 ml of 1% acetone/hexane. The second fraction was concentrated to 0.2 ml under the gentle stream of the pure nitrogen gas after addition of 10 ng of two internal standards (fluoranthene-*d*₁₂ and perylene-*d*₁₂).

PAHs compounds were analyzed on high resolution gas chromatograph /high resolution mass spectrometer (HRGC/HRMS, HP5890 /JEOL JMS700D) equipped with a HP-1MS capillary column (15 m × 0.25 mm i.d. × 0.25 μm film thickness). The injection port was kept at 300 °C, and a one μl of each concentrate was injected with splitless mode followed by 90 sec purge after injection. Column temperature was held at 70 °C for 1 min, then programmed at 15 °C/min to 130 °C, 6 °C/min to 300 °C, and held for 2 min.

RESULTS AND DISCUSSION

Particulate and gaseous total 65 PAHs concentrations (Σ 65PAHs)

The particulate and gaseous total 65 PAHs concentrations (Σ 65PAHs) were shown in Fig. 1. Averages of particulate and gaseous Σ 65PAHs were 63 ± 82 and 1200 ± 480 ng m⁻³, respectively. Among the locations, particulate and gaseous Σ 65PAHs at the location of No.9 near a bus and motorcycle terminal were the highest and their values were 290 and 2000 ng m⁻³, respectively. The gaseous PAHs were approximately 95% of the total ones.

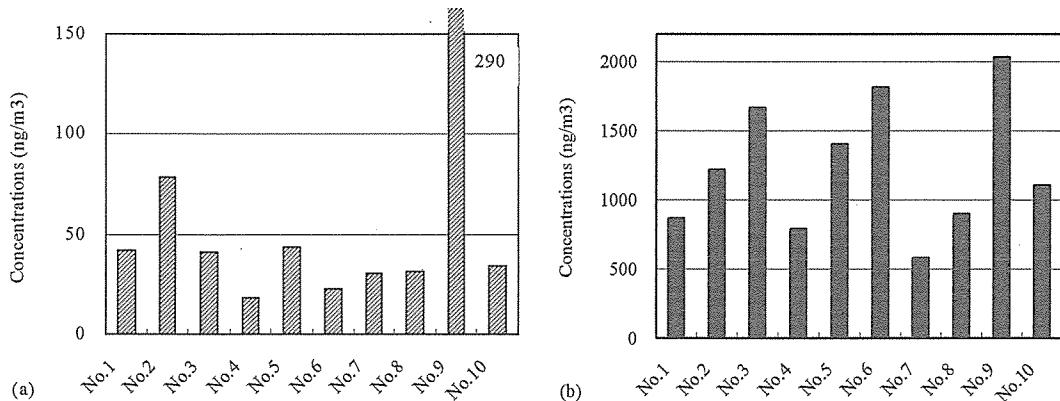


Fig. 1. Particulate (a) and gaseous (b) Σ 65PAHs at ten sampling locations

2 to 7 aromatic rings of PAHs

Averages of particulate and gaseous 2 to 7 aromatic rings of PAHs were shown in Fig. 2 and Fig. 3, respectively. Particulate PAHs mainly consist of 4 to 7 ring PAHs, whereas gaseous PAHs mainly consist of 2 to 4 ring PAHs.

Averages of particulate 4, 5, 6, and 7 ring PAHs were 9.0, 21, 22, and 8.6 ng m⁻³, respectively. Predominant categories were 6, 5, and 7 ring PAHs. However, the predominant categories at a location of No.9 was in the order of 5, 6, and 4 ring PAHs (145, 76, and 51 ng m⁻³).

In the case of gaseous PAHs, averages of

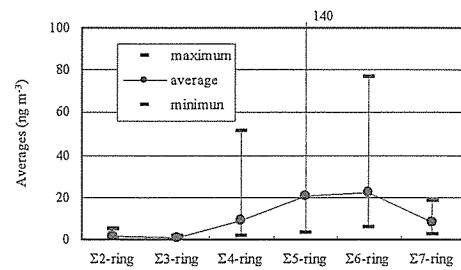


Fig. 2. Averages of particulate 2 to 7 ring PAHs

gaseous 2, 3, and 4 ring PAHs were 610, 460, and 170 ng m⁻³, respectively. Predominant categories were 2, 3, and 4 ring PAHs. However, the predominant categories at a location of No.9 were in order of 3, 4, and 2 ring (1000, 570, and 410 ng m⁻³).

These results suggested the existence of the specific emission sources around the location of No.9.

Components of the particulate and gaseous PAHs

The patterns of relative averages of twelve representative components of particulate PAHs were shown in Fig. 4. Among twelve components, the abundant components of particulate PAHs at nine locations were BghiP, coronene, and INcdP and their averages were 8.3, 7.7, and 7.5 ng m⁻³, respectively. The abundant components of particulate ones at the No.9 were BaP, INcdP, BkF, BbF/BjF, BghiP, chrysene/triphenylene, BeP, and coronene and their concentrations were 52, 37, 33, 30, 29, 27, 22, and 17 ng m⁻³, respectively.

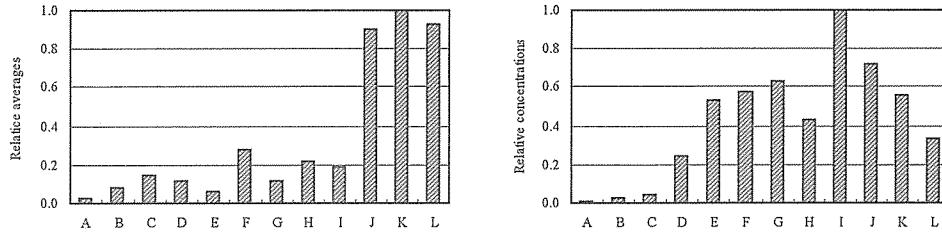


Fig. 4. Relative averages of twelve representative components of particulate PAHs.

Left side; the nine locations (No.1 to 8 and 10), Right side; No.9.

A; phenanthrene, B; fluoranthene, C; pyrene, D; BaA, E; triphenylene/chrysene, F; BbF/BjF, G; BkF, H; BeP, I; BaP, J; INcdP, K; BghiP, L; coronene.

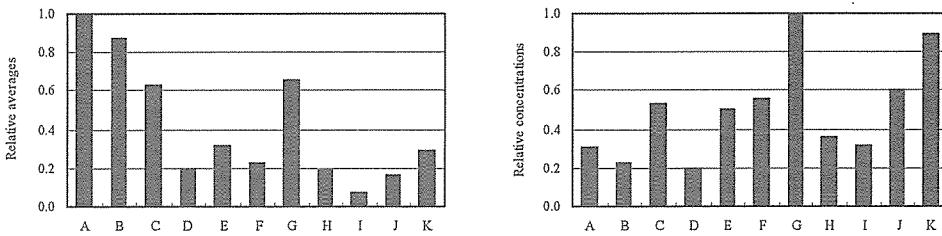


Fig. 5. Relative averages of eleven representative components of gaseous PAHs.

Left side; the nine locations (No.1 to 8 and 10), Right side; No.9.

A; naphthalene, B; methylnaphthalene isomers, C; dimethylnaphthalene isomers, D; 2,3,5-trimethylnaphthalene, E; acenaphthylene, F; fluorene, G; phenanthrene, H; methylphenanthrene isomers, I; anthracene, J; fluoranthene, K; pyrene.

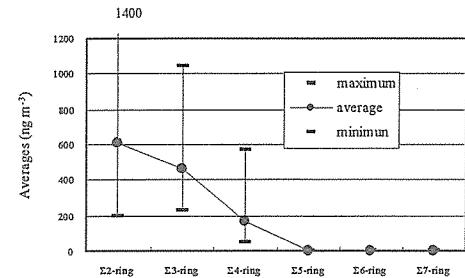


Fig. 3. Averages of gaseous 2 to 7 ring PAHs.

The patterns of relative averages of eleven representative components of gaseous PAHs were shown in Fig.5. Among eleven components, the abundant components of gaseous PAHs at nine locations were naphthalene, methylnaphthalene isomers, phenanthrene, dimethylnaphthalene isomers, acenaphthylene, pyrene, and fluorene and their averages were 220, 200, 150, 140, 71, 65, and 50 ng m^{-3} , respectively. On the other hand, the abundant components of gaseous ones at the No.9 were phenanthrene, pyrene, fluoranthene, fluorene, and acenaphthylene and the value was 300, 270, 180, 170, and 150 ng m^{-3} , respectively.

The patterns of representative components of particulate and gaseous PAHs at the No.9 were different from those at the nine locations. These facts also indicated that additional emission sources would exist at a location of No.9.

Estimation of emission sources of PAHs

Youngblood and Blumer (1975) reported that the origin of PAHs could be estimated from the ratio ($\Sigma\text{MPs}/\text{P}$) of sum of concentrations of methylphenanthrene isomers (ΣMPs) to that of phenanthrene (P). The ratio in the petrol (petrogenic origin) was more than 2.0, whereas that in the exhaust from the combustion process of the materials (pyrogenic origin) was less than 1.0. Each average of $\Sigma\text{MPs}/\text{P}$ of particulate and gaseous PAHs was 0.75 ± 0.20 , and 0.29 ± 0.04 , respectively. At a location of No.9, each $\Sigma\text{MPs}/\text{P}$ of those was 0.70 and 0.36, respectively. According to the criteria of the $\Sigma\text{MPs}/\text{P}$, the pollutions of particulate and gaseous PAHs would be mainly originated from the pyrogenic sources.

Yunker et al. (2002) had estimated the emission sources of PAHs on the basis of the ratio (fluoranthene/(fluoranthene+pyrene)) of fluoranthene to sum of fluoranthene and pyrene. The ratios of <0.2, 0.2-0.5, and >0.5 were corresponding to the petrogenic origin, the exhaust gases of gasoline and diesel engines, and the combustion of coal, grass, and wood, respectively. Each average of the ratios fluoranthene/(fluoranthene+pyrene) of particulate and gaseous PAHs was 0.35 ± 0.03 and 0.37 ± 0.02 , respectively. At a location of No.9, each ratio of those was 0.35 and 0.40, respectively. These values were close to that of the exhaust gas of gasoline and diesel engines.

Schuetzle and Frazier (1986) had estimated the emission sources by using the ratio of pyrene to BaP. The ratios of pyrene/BaP in exhaust gases of diesel engines were close to 13, and those in exhaust gases of gasoline engines were approximately one-tenth of those in exhaust gases of diesel engines. An average of pyrene/BaP of particulate PAHs was 0.83 ± 0.46 . The value was close to those of the exhaust gas of gasoline engines.

Rogge et al. (1993) reported that BghiP and coronene among components of particulate PAHs exhausted from the noncatalyst automobiles were the most abundant. The ratios (coronene/(coronene+BghiP)) of coronene to sum of coronene and BghiP of exhaust gas from non-catalytic automobiles was calculated to be 0.42, whereas those of exhaust gas from catalyst-equipped automobiles was calculated to be 0.19. The average of coronene/(coronene+BghiP) was 0.46 ± 0.04 . On the contrary, the average of coronene/(coronene+BghiP) in Osaka was 0.29 ± 0.07 (Kishida et al., 2006). These results suggested that the gasoline engines without catalytic converter have been popular in Hanoi.

At a location of No.9, the ratio of pyrene/BaP was 0.04 because of the high concentration (52 ng m^{-3}) of BaP in particulate PAHs. An average of BaP at the nine locations (No.1 to 8 and 10) was $1.6 \pm 1.0 \text{ ng m}^{-3}$. These results indicated that atmospheric PAHs were mainly emitted from noncatalyst automobiles. Another emission sources would be expected to exist at a location of No.9.

CONCLUSIONS

A survey on sixty five components of PAHs contained in PM and in gas phase was conducted in Hanoi. Particulate and gaseous PAHs were collected on the QFF and on the PUF plugs, respectively. Averages of particulate and gaseous $\Sigma 65\text{PAHs}$ were 63 ± 82 and $1200 \pm 480 \text{ ng m}^{-3}$, respectively. The highest values of the particulate and gaseous ones observed at a location of No.9

were 290 and 2000 ng m⁻³, respectively. The values of gaseous PAHs were approximately 20 times higher than those of particulate ones.

From the estimation of specific components of PAHs, the pollutions of PAHs were originated from the pyrogenic sources. Among pyrogenic sources, the exhaust gases from noncatalyst automobiles mainly contributed to the pollution of PAHs. Another emission sources would be expected to exist at a location of No.9.

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