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DIURNAL CHANGE OF PAHs AND NITRO-PAHs IN THE ATMOSPHERIC PARTICULATE MATTER AT THE ROADSIDE IN HO CHI MINH CITY, VIETNAM

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Abstract

Measurements of five polycyclic aromatic hydrocarbons (PAHs) and two nitro-PAHs were carried out at a traffic point of Ho Chi Minh City, Vietnam. 1-nitropyrene (1-NP) and 2-nitrofluoranthene (2-NF) were chosen as representative nitro-PAHs primarily emitted and secondarily generated. Atmospheric concentrations of PAHs and nitro-PAHs are of interest because both of these compounds including mutagens and carcinogens. Samples of particulate matter were collected in five periods per day in July 2006 at the roadside of the city. The aim of this work is to survey the diurnal variation and contribution of PAHs and nitro-PAHs in the particulate matter. The analytical results in this study showed that the particle-phase pollution of PAHs and 1-NP was so high at the roadside, especially the concentration of Benzo[a]pyrene ranged from 5.1 to 18.5 ng m⁻³. The occurrence of 2-NF at the roadside is a proof of gas phase formation in the atmosphere.

Keywords: PAHs, nitro-PAHs, particulate matter, roadside, Ho Chi Minh City.

1. Introduction

PAHs and nitro-PAHs are of special concern due to their toxicity (carcinogenicity, mutagenicity, estrogen disturbance) to human beings (Tokiwa et al., 1994; Durant et al., 1996; Hannigan et al., 1998). Nitro-PAHs are derivatives of PAHs that are emitted from the incomplete combustion of organic materials. Additionally, nitro-PAHs are also formed in the atmosphere via reaction of their parent PAHs with OH and NO₃ radicals in the gas phase (Arey et al., 1986; Pitts Jr. et al., 1978; Atkinson et al., 1990) and/or the heterogeneous gas-particle interaction of the parent PAHs adsorbed onto particles with nitrating agents (Feilberg et al., 2001). 2-nitrofluoranthene can also be formed by the gaseous phase reaction of fluoranthene with nitrate radicals (NO₃) at night (Atkinson and Arey, 1994; Arey and Atkinson, 2003). 1-NP is believed to be mainly emitted directly from diesel exhaust.

In the atmosphere, PAHs and nitro-PAHs with two aromatic rings were detected only in the vapor phase, while PAHs and nitro-PAHs with three-ring were found in both the gas and particle phases and the compounds with four or more rings were mainly in particles (Dimashki et al., 2000; Reisen and Arey, 2005). Nitro-PAHs are generally found in the atmosphere at very low concentrations compared to their parent PAHs (Feilberg et al., 2001). However, some nitro-PAHs exhibit higher mutagenicity and carcinogenicity in microbial mutagenicity bioassays and in forward mutation assays based on human cells than their parent PAHs (Pitts Jr. et al., 1978, Durant et al., 1996).

In the previous report, we have investigate the seasonal and daytime/nighttime variations of PAHs in the particulate matter at the ambient air in Ho Chi Minh City. Besides, nitro-PAHs have been investigated in order to know their occurrence and emission sources in the atmosphere. In this study, the particulate matter was collected five time periods per day that aims to understand the diurnal change of PAHs and nitro-PAHs at the roadside.

2. Methods

2.1. Sampling site and sample collection

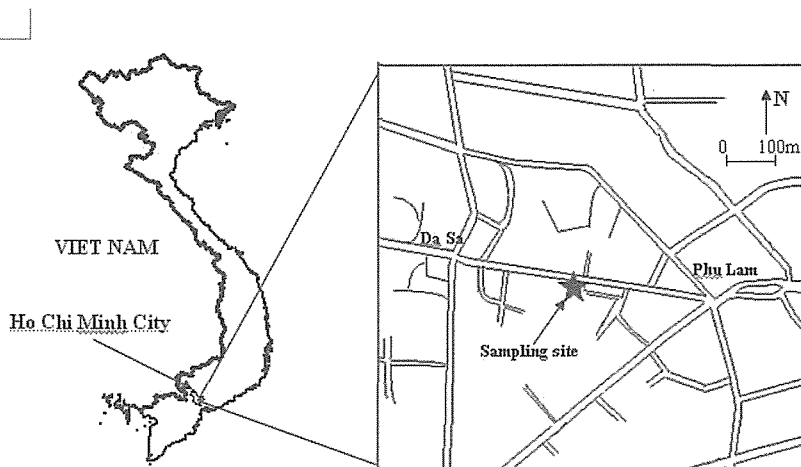


Figure 1. Map of the sampling site in the urban area of HCMC, Vietnam

Particulate matter was collected on a quartz fiber filter using a high volume air sampler (Kimoto Electric Co., Model 120H) at flow rate of 800 L min^{-1} . The particulate matter was collected at the rooftop of a residential house ($10^{\circ}45'19'' \text{ N}$, $106^{\circ}37'43'' \text{ E}$) located on a busy street which is the major connection and in the middle of the four-road junction Da Sa and the five-road roundabout Phu Lam about 300 m from both traffic junctions with unique transportation, that is, motorcycles, trucks, cars and buses (Figure 1). The sampling inlet was set 4 m above the ground level. The sampling was done in July 2006.

2.2. PAHs and Nitro-PAHs analysis

Prior to high-performance liquid chromatography (HPLC) analysis, PAHs and nitro-PAHs on the filters were extracted by ultrasonication for 20 min in the solvent benzene/ethanol (3/1 v/v), and the solution was filtered with a cellulose acetate filter (Advantec MFS, No.2) to remove solid substances. The filtrate was cleaned with 100 mL of 5% NaOH, followed by 100 mL of 20% H_2SO_4 and then 100 mL of Millipore water. The extract was concentrated to about 3 mL by a rotary evaporator and was evaporated almost to dryness with a gentle stream of nitrogen. The residue was finally dissolved in 0.5 mL of methanol. The extract, after passing through a $0.22 \mu\text{m}$ filter, was injected into the HPLC system for PAHs and nitro-PAH analysis.

Five PAHs Benzo[*e*]pyrene (BeP), Benzo[*b*]fluoranthene (BbF), Benzo[*k*]fluoranthene (BkF), Benzo[*a*]pyrene (BaP) and Benzo[*ghi*]perylene (BghiP) were analyzed by using a High Performance Liquid Chromatography (HPLC) with fluorescence detection.

The presence of two nitro-PAHs, 1-NP and 2-NF, was determined by using HPLC with chemiluminescence detection and column-switching according to the procedure described in previous studies with some modifications (Murahashi and Hayakawa, 1997; Hayakawa *et al.*, 2001). The system consists of four HPLC columns, a separation column (Inertsil ODS-3; 4.6 mm i.d.×150 mm), a reduction column (NPPak-RS, Jasco, 4.0 mm i.d.×10 mm), a concentration column (Inertsil ODS-3; 4.0 mm i.d.×10 mm), an analytical column (Inertsil ODS-3; 4.6 mm i.d.× 250 mm), and a chemiluminescence detector (Jasco FP-2020 with CLKIT C454). An acetonitrile solution containing

0.04 mM bis(2,4,6-trichlorophenyl)oxalate and 30 mM hydrogen peroxide was used as a chemiluminescence reagent. The mobile phase for the analytical column was a mixture of imidazole-HClO₄ buffer (pH 7.6) - acetonitrile (40/60 v/v) and the mobile phase for the separation and reduction columns was a methanol/water mixture (75/25 v/v).

3. Results and discussion

3.1. Diurnal change of PAHs concentrations

Concentration measurements of PAHs and nitro-PAHs were carried out over five-day periods at the sampling site. Samples were collected in five periods per day: 06.00h – 10.00h, 10.10h – 14.10h, 14:20 h – 18.20 h, 18:30 h – 23:30 h, 23:40 h – 05:40 h, local time in July 2006. Diurnal change of the concentrations of five PAHs is shown in Figure 2.

In general, the diurnal changes of each PAH were quite similar. The lowest concentration was observed in the 23:40 h – 05:40 h samples. The concentration of PAHs in the samples from 10:10 h – 14:10 h were lower than those in other samples in the daytime. The highest concentration was observed for BghiP. As described above, the sampling site is on the busy road with a relatively high traffic density, therefore PAHs are the main components emitted directly from vehicular exhaust, particularly gasoline and diesel powered vehicles. Thus, the variation of PAHs with the time depends mainly on the amount of vehicles. From the midnight, the amount of vehicles was minimum therefore the concentrations of PAHs were lowest. At noon, from 10:10 h – 14:10 h, the concentration of PAHs decreased due to decomposition of PAHs under high temperature and strong solar radiation.

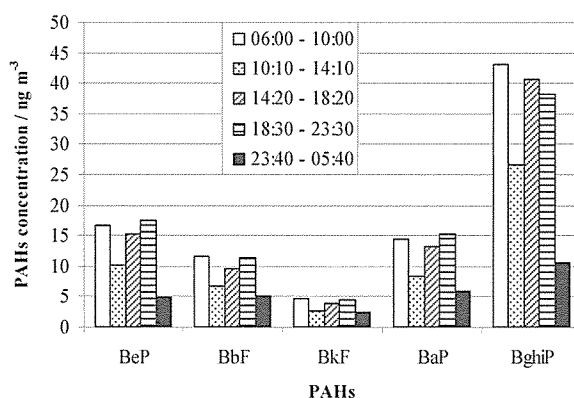


Figure 2. Diurnal variations of individual PAHs at the roadside in Ho Chi Minh City, 2006.

One issue of social concern is the potentially carcinogenic PAHs that have an influence on human health. BaP, BghiP, BbF, and BkF were reported to account for most of the mutagenic potency in human cells and are indicators of cancer risk for humans in which BaP is the strongest carcinogenic compound (Hannigan et al., 1998; Kameda et al., 2005). The concentrations of these PAHs were different at different time per day. The concentration of BaP at the sampling site ranged from 5.1 to 18.5 ng m⁻³. BaP average concentration levels observed are much higher than those observed in the atmosphere at ambient air in Ho Chi Minh City in our other study (BaP: 0.11–2.0 ng m⁻³) (Hien et al., 2007a). BaP is currently estimated to be the most toxic of the PAH compounds found in the environment so far. Even though it has been generally found in modest concentrations, BaP is the largest contributor to overall toxicity (EPA, 2002). In general, no ambient air quality standards have

been set for PAHs. However, proposals and guidelines have been announced for BaP in Europe. The UK has proposed an annual average goal of 0.25 ng m^{-3} for BaP by 2010. Previously, the European Commission has recommended a limit value between 0.5 and 1.0 ng m^{-3} for BaP for 2005 (EPA, 2002). The concentration of BaP in this study exceeds the UK Standard. High concentrations of BaP is an alarming signal for air pollution issues in Ho Chi Minh City. These results may provide strong evidence of a cause for increasingly high rates of lung and skin disease in inhabitants of Ho Chi Minh City in recent years.

3.2. Diurnal change of 1-NP and 2-NF concentrations

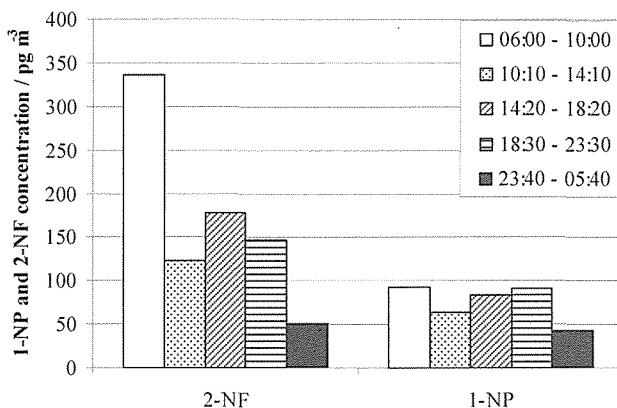


Figure 3. Diurnal variations of 1-NP and 2-NF at the roadside in Ho Chi Minh City, 2006.

Concentrations of 1-NP and 2-NF in the particulate matter were shown in Figure 3. The concentrations of 1-NP and 2-NF changed with the time of the day. In the day time, the concentration of 2-NF was highest in the morning from 06:00 h – 10:00 h and was lowest from 10:10 h – 14:10 h. At night, the concentrations of 2-NF from 18:30 h to 23:30 h were higher than those from 23:40 h to 05:40 h. As mentioned above, 1-NP is believed to be mainly emitted directly from diesel exhaust, whereas 2-NF is considered to be formed as the product of the gas-phase reaction of either OH or NO₃ radicals with Fluoranthene in the presence of NO₂. 2-NF concentration was dominant in both nitro-PAHs investigated. The abundance of 2-NF in the morning suggests that the reaction of OH radical with Fluoranthene in the gaseous phase plays an important role in the formation of 2-NF at the traffic site. This might be due to the high concentration of OH radicals in the morning at the traffic site. Photolysis of nitrous acid (HONO) may be an important source of OH radicals ($\text{HONO} + h\nu (\lambda < 370 \text{ nm}) \rightarrow \text{OH} + \text{NO}$) in the early morning (Harris et al., 1982) at this site, which is directly emitted from vehicular emissions (Pitts Jr. et al., 1984). This result is consistent with our previous results (Hien et al., 2007b). The lower concentration in the afternoon from 10:10 to 14:10 might be due to the decomposition of 2-NF during this time. The average concentration of 2-NF in the daytime was higher than at nighttime. These results implicate that the occurrence of 2-NF at the sampling site is the proof of its atmospheric formation.

As for 1-NP, at each time period, the concentrations of 1-NP was lower than those of 2-NF. The concentration of 1-NP was no big difference during the daytime. The lower concentration of 1-NP in the afternoon from 10:10 h to 14:10 h may be due to photodecomposition of 1-NP during the daytime. The concentrations of 1-NP at this sampling site were so high compared to those at the ambient air (Hien et al., 2007b). The presence of 1-NP at the roadside is a marker for diesel engine exhaust in the atmosphere in Ho Chi Minh City.

4. Conclusions

The results in this study indicated the diurnal change of PAHs, 1-NP and 2-NF at the roadside in Ho Chi Minh City. The concentration of PAHs and 1-NP changed with the time depending mainly on the amounts of vehicles. The concentration of 2-NF was highest in the morning and lowest from midnight. The concentration of BaP was very high at the sampling site. Further studies on these compounds need to be implemented, especially studies on fine particles smaller than 2.5 μm that can enter easily the human body through inhalation.

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