Polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons in urban air particulate matter in Ho Chi Minh City, Viet Nam

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ABSTRACT

Particulate matter (PM) was collected in ambient air and at the roadside in urban air in Ho Chi Minh City. Both polycyclic aromatic hydrocarbons (PAHs) and nitro-polycyclic aromatic hydrocarbons (NPAHs) were determined in the extract from particulate matter using a HPLC with fluorescence and chemiluminescence detection. PM, PAHs, and NPAHs concentrations collected in the ambient air were lower than those at the roadside. BghiP was the most abundant. The concentration of 2-NF was higher than 1-NP at both sampling sites. The ratio of 2NF/1-NP in the ambient air was higher than that at the roadside. The gas-phase formation of 2-NF was very important in the atmosphere. PAHs and two NPAHs were mainly associated with fine particles smaller than 2.1 μm. Vehicular emission is main source of PAHs and NPAHs in the particulate matter in the atmosphere in Ho Chi Minh City.

Keywords: PAHs, NPAHs, particulate matter, Ho Chi Minh City.

INTRODUCTION

Atmospheric environment in urban areas contains numerous kinds of organic pollutants. Among them, polycyclic aromatic hydrocarbons (PAHs) and nitro-polycyclic aromatic hydrocarbons (NPAHs) are of special concern due to their toxicity (carcinogenicity, mutagenicity, estrogen disturbance) to experimental animals (Finlayson-Pitts and Pitts Jr., 1997). NPAHs are derivatives of PAHs. PAHs and NPAHs are emitted from incomplete combustion processes of organic materials. Besides, NPAHs are also formed via reaction of their parent PAHs with OH and NO_3 radicals in the gas phase and/or heterogeneous gas–particle interaction of parent PAHs adsorbed onto particles with nitrating agents. PAHs and NPAHs were found in gasoline and diesel exhaust particles and in the atmospheric particulate matter (Bamford et al., 2003; Reisen and Arey, 2005). NPAHs are generally found in the atmosphere in concentration of 10–1000 times lower than their unsubstituted parent PAHs (Feiberg et al., 2001), however some certain NPAHs exhibit higher mutagenicity (2×10^5 times) and carcinogenicity (10 times) in a microbial mutagenicity bioassays and in a forward mutation assay based on human cells compared to parent PAHs (Pitts et al., 1978, Lewtas and Nishioka, 1990; Lewtas et al., 1990; Durant et al., 1996). NPAHs with 4 rings such as 1-nitropyrene (1-NP) and 2-nitrofluoranthene (2-NF) (derivatives of pyrene and fluoranthene, respectively) are the most abundant among NPAHs found in the air environment.

In the last years, Vietnam's explosive economic growth has reduced poverty and

improved the quality of life for millions. At the same time, this unprecedented urban and industrial development has come at the expense of air quality, particularly in densely populated urban centers. Major cities in Viet Nam, especially Ha Noi and Ho Chi Minh City, are experiencing serious air pollution problems. Motor vehicles are the principal cause of this pollution. Several studies have concentrated on the inorganic components in the particulate matter (Hien et al., 2001) and the concentrations of air pollutants such as sulfur dioxide, nitrogen oxides, ammonia in the ambient air (Lan et al., 2004). However, the information of organic components in the particulate matter such as PAHs and especially NPAHs is scare. In this study, particulate matter was collected in the atmosphere in Ho Chi Minh City and PAHs and NPAHs in the particulate matter were determined.

EXPERIMENTAL METHOD

Sampling

Particulate matter was collected on a quartz fiber filter using a high volume air sampler (Kimoto Electric Co., Model 120H) at flow rate of 1000 L min^{-1}. The sampler was placed on a three-storey building at University of Natural Sciences, Viet Nam National University. This sampling site is located in residential areas regarded as the ambient air in Ho Chi Minh City. The sampling was done from Jan. 2005 to Mar. 2006.

Besides, particulate matter was also collected at the roadside in Ho Chi Minh City using a low pressure cascade impactor (Kanomax, Model 3551). The sampling was carried out every week in working days from Jan.17 to Feb. 5, 2005 and from Jul. 4 to 29, 2005 at flow rate of 28.3 L min^{-1}. Particles were separated into nine fractions, consisting of 8 stages in size ranges > 9.0 ; 9.0–5.8; 5.8–4.7; 4.7–3.3; 3.3–2.1; 2.1–1.1; 1.1–0.7; 0.7–0.4 μm, and a final filter collecting particles smaller than 0.4 μm.

PAHs and NPAHs analysis

PAHs and NPAHs on the filters were extracted by sonication in the solvent benzene/ethanol (3/1 v/v). 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 to almost 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 μm filter, was injected into the HPLC system for PAHs and NPAHs analysis.

Eleven PAHs (Fluoranthene (Fluo), Pyrene (Py), Triphenylene (Tri), Benzo[*a*]anthracene (BaA), Chrysene (Chr), Benzo[*e*]pyrene (BeP), Benzo[*b*]fluoranthene (BbF), Benzo[*k*]fluoranthene (BkF), Benzo[*a*]pyrene (BaP), Benzo[*ghi*]perylene (BghiP) and Indeno[1,2,3-*cd*]pyrene (InP)) were analyzed by using a high performance liquid chromatography (HPLC) with fluorescence detection. For the samples collected by a low pressure cascade impactor, BeP was not determined.

Two NPAHs, 1-nitropyrene (1-NP) and 2-nitrofluoranthene (2-NF), were determined by using a HPLC with chemiluminescence detection reported by Hayakawa et al., 2001 with some modifications.

RESULTS AND DISCUSSION

Table 1 and Fig.1 show the concentration levels of PM, total PAHs and NPAHs (1-NP

and 2-NF) associated with particles in the atmosphere at ambient air and at the roadside in Ho Chi Minh City during sampling period. The sum of concentrations of 11 PAHs is abbreviated as total PAHs. The average concentration values of all individual PAHs and NPAHs species and PM in the ambient air were much lower than those at the roadside. PM at the roadside exceeds Vietnamese Air Quality Standard (200 $\mu g\ m^{-3}$). The total of concentrations of PAHs with four aromatic rings (Fluo, Py, Tri, Chr) were lower than that of PAHs with 5 rings (BeP, BbF, BkF, BaP) and 6 rings (BghiP, InP). Large differences in the concentration of PAHs found between the ambient and roadside air in this study indicate that traffic is an important source of PAHs contributing to airborne particles. Besides, BghiP was the most abundant among PAHs investigated at two sites. Benzo[ghi]perylene can be used as a marker of gasoline powered vehicle activity (Mar et al., 1999), therefore this result suggests that gasoline-powered vehicles are an especially significant source of PAHs in the atmosphere in Ho Chi Minh City.

Table 1. The concentration of PM, some PAHs and NPAHs at two sampling sites

Compound ($pg\ m^{-3}$)	Ambient air n=60	Roadside n=7
1-NP	8.11 ± 4.12	60.5 ± 20.1
2-NF	136 ± 66.8	313 ± 105
Pyrene	249 ± 138	5080 ± 2040
Fluoranthene	254 ± 121	3650 ± 759
Total PAHs	7570 ± 3770	55600 ± 13800
PM, $\mu g\ m^{-3}$	100 ± 28.2	434 ± 66.0

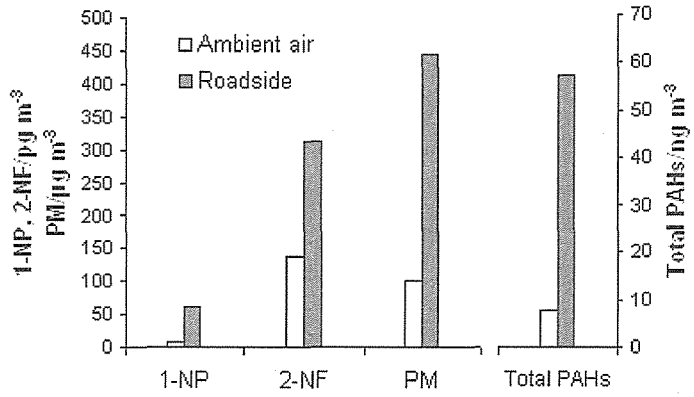

Fig. 1. The average concentrations of PM, PAHs and NPAHs

The concentrations of 1-NP and 2-NF were lower than their parent PAHs, pyrene and fluoranthene (Table 1). 2-NF was the most abundant particle-associated NPAHs, and lower levels of 1-NP. The amounts of 2-NF in samples collected in ambient air were much higher than 1-NP compared to those at the roadside. It is well known that 1-NP is emitted directly from incomplete combustion processes and its presence in ambient air samples is a sign of pollution by diesel vehicle traffic. While 2-NF is mainly formed in

the gas phase via reaction of fluoranthene with OH and NO_3 radicals and the gas-phase 2-NF deposits on particles immediately afterward. In this study, the average ratios of 2-NF/1-NP in the samples collected in ambient air were significantly higher than those in the samples at the roadside. This result indicates that the gas-phase information of 2-nitrofluoranthene is very important in the atmosphere. Besides, the high concentration of 1-NP in the samples at the roadside and also in the ambient air indicates that the diesel emission is a significant source of NPAHs in the atmosphere.

In addition, the concentrations of all PAHs and NPAHs investigated in this study increased with the decrease in particle size and were found to be the most abundant in PM smaller than 0.4 μm (Fig. 2). There are approximately 80% of total PAHs, 71 % of 2-NF, and 76 % of 1-NP found in fine particles smaller than 2.1 μm. It should be noted that these fine particles are really dangerous particles because they can penetrate deeply into the cells and blood vessels of the lung. Among PAHs and NPAHs found in the atmosphere, BaP, BghiP, BbF, InP, and BkF exhibit high toxicity, and, especially 2-NF exhibits very high mutagenicity and carcinogenicity. The result in this study gives important information about pollution levels of PAHs and NPAHs associated with particulate matter in Ho Chi Minh City.

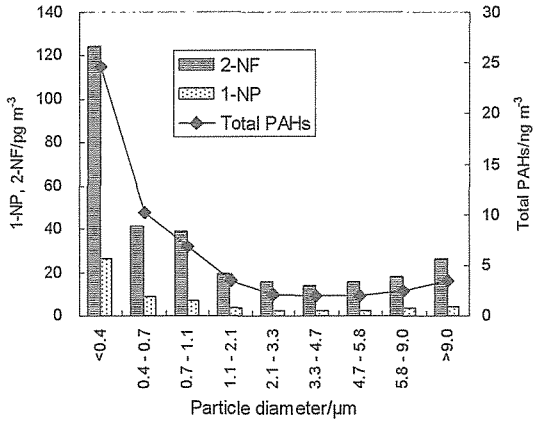

Fig. 2. The distribution of PAHs and NPAHs concentrations with different particle sizes in PM at the roadside in Ho Chi Minh City

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