CONTRIBUTION ESTIMATE OF PAHS TOXIC COMPOUNDS IN AIR ENVIRONMENT AT MAJOR TRAFFIC JOINTS OF HANOI, VIETNAM

Pham Hung Viet[1], Nguyen Thuy Ngoc[1], Nguyen Thi Hanh[1], Nguyen Minh Son[1], Luong Manh Tuan[1], Vo Thanh Le[1] and Yasuaki Maeda[2]

[1] Research Centre of Environmental Technology and Sustainable Development (CETASD) Hanoi University of Science, Vietnam. [2] College of Engineering, Osaka Prefecture University, Japan

ABSTRACT

Sixteen most relevant polycyclic aromatic hydrocarbons (PAHs) components, which EPA proclaimed, were measured by collection of dust samples in Hanoi, Viet Nam. The street dust samples in air were collected at many important traffic joints in both rainy seasons in 2002, dry season in 2003 and one blank sample from reserve forest as a reference sample. It was observed that the sums of PAHs concentrations were ranged from 3.34 to 182.8 ng/m^3 in rainy season and from 6.1 to 135.2 ng/m^3 in dry season, respectively. All analytical results showed that traffic joints in Hanoi have been high polluted by concentrations of 4-ring to 6-ring PAHs. The highest PAHs concentration was So crossroad both in two seasons, 182.8 ng/m^3 in rainy season and 135.2 ng/m^3 in dry season. And the ambient air concentration of Benzo(a)pyrene (BaP) was also evaluated highest at So crossroads were 11.58 and 8.54 ng/m^3, respectively.

INTRODUCTION

Hanoi located in the North of Vietnam has an area of 927.9 km^2 and a population of 3.5 millions. Sixty-two percents of Hanoi population have to transport commonly. Nowadays, the transportation of city is not suitable with citizen demands. Because public traffic is not convenient and Vietnamese habit is using personal means of transport, so there are a large number of personal transport vehicle in city. Hanoi has 1.2 millions motorbikes and more 100 thousands automobiles (statistic in 2001, Vietnamese Ministry of Transportation) and not including a large number of vehicles from suburban and neighbour provinces come to center of city daily. The major character of streets in Hanoi is small and having many road-joints, the surrounding roads of city are being conducted and widened and a little overpasses. The traffic jams not only happen in the rush hours at crossroads and T-junctions but also happen at any time whenever the streets get troubles. Therefore, the emission of exhaust gas became the most intensive at these points.

Polycyclic aromatic hydrocarbons are one of the most serious pollutants because of their carcinogenicity and mutagenicity. Exhaust gases of motor vehicles using gasoline, diesel fuels contain many non-polar polycyclic aromatic hydrocarbons (PAHs) such as Benzo (a) pyrene (BaP). PAHs are generally formed in incomplete combustion of organic material. In ambient air PAHs exist in both gas phase and particulate matter, therefore their existence has a direct impact on the human population. The epidemiology evidence illustrated that high PAHs concentration at urbanization areas relates closely to increasing lung cancer risk [2]. Consequently, it is necessary and urgent to determine the trace levels of PAH in air environment at traffic joints in metropolitan cities like Hanoi.

Until now there are still almost no results and data about PAH levels in atmosphere in Vietnam especially at traffic points. This investigation is a primary research of PAH concentrations in air environment at the important traffic points in Hanoi. Sixteen most relevant PAH components, which EPA proclaimed, were measured by collection of dust samples at Hanoi and one dust sample was collected at Cuc Phuong forest (more 100 km far from Hanoi) which can be considered as pristine and reference area.

EXPERIMENTS

Materials

Reagents and solvents (methanol, dichloromethane, n-hexane and acetone) used for PAHs extraction from dust samples of analytical grades (Merck AG).
Individual standards of PAHs are crystals, were bought from EQ, Dr.Ehrenstorfer GmbH Co. (Germany). The standard stock solutions were prepared in acetone at concentrations of 0.5-1 mg/ml. Solution of internal standard IS (Chrysene - d_{12}) and surrogate compound (Benzo[a]pyrene - d_{12}) were prepared both of 0.1 mg/mL.
Whatman filter paper, GF/F grade (d.47mm) was used to filtrate the dust particles having diameter larger than 0.7μm.

Sampling sites

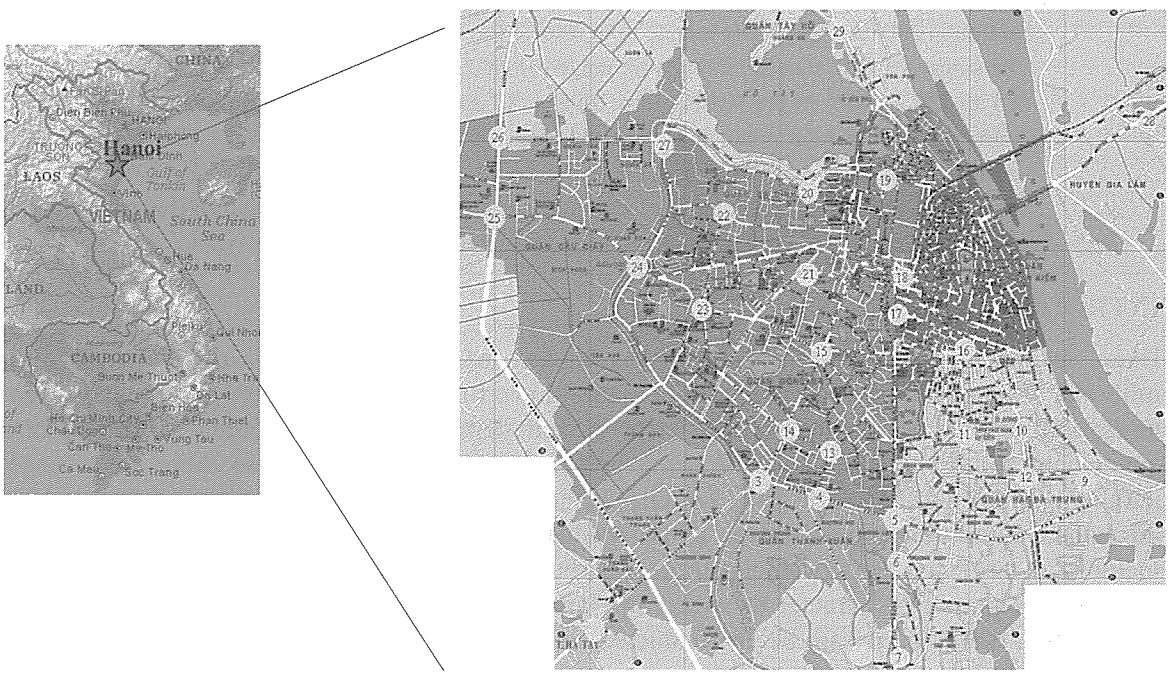
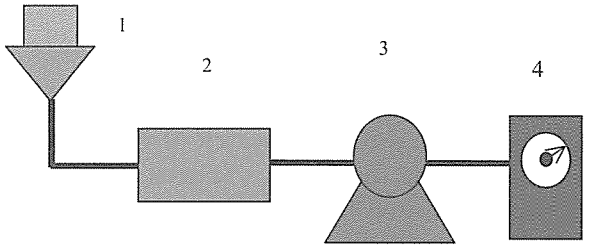


Figure 1. Some sampling sites in Hanoi

The air dust samples were collected at 43 points in rainy season from April to July, 2002 and 29 points in dry season, from December 2002 to March 2003 in the urban area. These are sites where frequency of motor vehicles is relatively high (see Fig.1).
One reference sample was collected at Cuc Phuong forest. There are almost no traffic and other artificial activities (e.g. biomass burning).

Sample collection



1. Filter
2. Air flow controller
3. Pump
4. Air flow meter

Figure 2. Air sampling equipment

The air dust samples were duplicated. The dust samples were collected by low volume pump ULVAC, DA-3OS (Japan) with 35W capacity using Whatman filters GF/F grade, which was activated in prior at 200^0C for 2 hours. The sampling time was always taken for 12 hours in daily with sampling flow of 24 L/min. Two filters were placed 1.5-2m above the ground bottom. After sampling, the filters were stored in fridge until analysing.

Sample preparations

In order to have a relatively fast extraction of PAHs from collected dust samples using only small amount of consumed chemicals, so the ultrasonic method was chosen. The chosen ultrasonic extraction is the one applying ultrasound waves (20 Hz frequency) to change associated affinity of PAH components and dust particles on the filter. Using a suitable solvent, the PAH compounds could be separated from dust surface and going into solvent phase.

The filter was cut to small pieces, put into glass 25mL tube with topper. Add SR standard Benzo (a) Pyrene-d12 and extract by ultrasonic with 10mL of mixture of dichloromethane (DCM) and n-hexane (1/1:v/v) for 15 minutes. Repeat the extraction step twice again for each sample. The extracted liquids were combined after three extraction times and concentrated to 1mL by vacuum evaporator. Next, the sample was cleaned-up through the silica gel cartridge LC-Si 500mg/3mL (Merck). The PAH components were eluted by solvent mixture of n-hexane and DCM. Then, the eluted solution was concentrated by nitrogen gas. Add IS standard solution Chrysen-d12, fill up to 1mL by n-hexane and inject 1µl into GC-MS.

The flow chart of sample preparation by ultrasonic can be described, as follows:

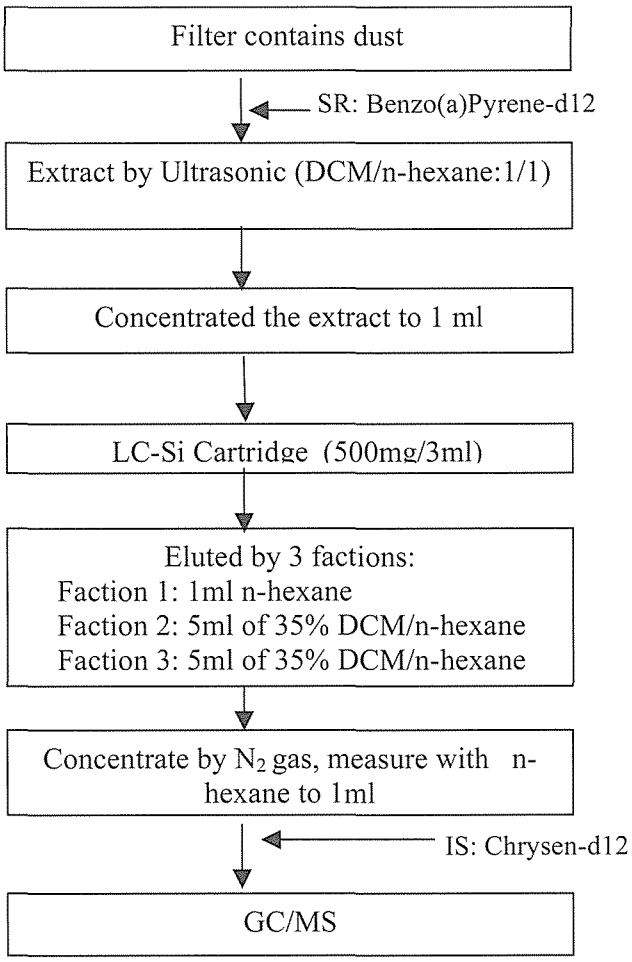


Figure 3. Flow chart of dust sample preparation

Analysis of PAHs Samples

The PAHs compounds were identified and quantified by a GC 17/MS-QP 5000, Shimadzu (Japan). The used gas chromatography (GC) was equipped with a 30m x 0.3mm id DB5 bonded phase fused silica capillary column (J & W Scientific, USA).

The helium carrier gas flow rate was 1.5mL/min. The injector temperature was 300^0C at a splitless mode. The interface temperature was 300^0C. A quantitative analysis was performed using selective ion monitoring (SIM) method at electron energy of 70eV and detector voltage

of 1.5kV. The oven temperature was held at 50^0C and then programmed to 100^0C at 25^0C/min and 300^0C at 8^0C/min and finally held isothermally at 300^0C for 15 minutes.
Before analysis real samples, we carried out qualitative analysis for the identification of the individual PAHs by GC/MS system. Determinate parameters of 16 PAHs are retention time, target ion and reference ion. The detection limits of instrument for 16 selected PAHs were ranged from 1.7÷ 6.7 ng/ml (in the last research).

RESULTS AND DISCUSSION

The PAHs concentrations in air environment at Hanoi traffic joints

In general, the obtained results showed that air ambient concentrations of PAHs in dry season were higher than rainy season. The average concentrations of PAHs at observed important traffic joints in Hanoi were measured at 26.68 ng/m^3 (n=43) in rainy season and 31.75 ng/m^3 (n=29) in dry season. In summer, from April to July, 2002 corresponding to rainy season, the daily temperature is almost more than 30°C. Therefore PAHs compounds, specially the volatile PAHs will easily diffuse into atmosphere. Furthermore, the continuous rain events cause the atmosphere is more clear and fresher at urbanization cities. Dust and polluted organic and inorganic compounds will be deposited and washed into ground by rain water. So that the PAHs amounts of the street air environment in Hanoi were larger in dry season.

Table 1. The concentration of 16 PAHs in atmosphere at Hanoi's traffic joints (ng/m3)

No.	Compound	Rainy season (n=43)		Dry season (n=29)	
		mean value	range	mean value	range
1	Napthalene	4.09	<0.1 - 49.10	0.60	<0.1 - 2.24
2	Acenaphthylene	0.51	<0.2 - 6.04	0.28	<0.2 - 0.37
3	Acenaphthene	0.47	<0.1 - 4.03	0.40	<0.1 - 0.62
4	Fluorene	0.88	<0.1 - 7.41	0.13	<0.1 - 0.59
5	Phenanthrene	0.88	<0.1 - 7.12	1.13	0.2 - 6.36
6	Anthracene	1.31	<0.1- 18.65	0.16	<0,2 - 0.84
7	Fluoranthene	0.81	<0.1-6.83	2.85	0.5 - 19.70
8	Pyrene	0.90	0.15-6.24	3.84	0.5 - 30.88
9	Benzo(a)anthre	1.18	<0.2-17.42	1.56	0.2 - 7.59
10	Chrysene	1.42	<0.2-14.72	2.63	0.5 - 11.06
11	Benzo(b)Fluoran	3.41	<0.3-25.34	5.13	1.2 - 17.6
12	Benzo(k) Fluoran	2.31	0.3-20.18	1.17	0.2 - 3.85
13	Benzo(a) Pyrene	1.47	<0.3-13.40	2.21	0.4 - 8.54
14	Indeno(1,2,3-cd)py	2.11	<0.3-14.00	3.40	0.8 - 9.88
15	Dibenzo(a,h)anth	2.25	<0.3-40.96	0.55	<0.3 - 1.25
16	Benzo(g,h,i)pery	2.68	<0.3-19.92	7.09	1.1 - 23.84
	Total:	**26.68**	**2.80-182.80**	**31.75**	**6.10 - 135.22**

The comparison of PAHs concentrations at the observed traffic joints in both seasons in Hanoi, many sites had total PAHs were higher in dry season or approximately amounts. Except some traffic points, their concentrations of PAHs were decreased in compare with rainy season.
In the rainy season from April to July 2002, three most interested traffic joints with over 100 ng/m^3 of PAHs concentrations in street air environment were So crossroad (HN3), Vong (HN5) crossroads and La Thanh dike- Nguyen Chi Thanh snarl (HN23). They were the most crowed traffic points of Hanoi with high transportation frequency of different kinds of motor vehicles and traffic jams also happen daily.

In the end of 2002 and the beginning of 2003, Hanoi government had many methods to solve and overcome the traffic problems of Hanoi transportation. There were some opened streets, building the overpass bridge at traffic points with overload number of motor vehicles, the sense of urban people are better in executing traffic law. Two of three the most concerned traffic points in 2002, the total PAHs concentration were reduced considerably at Vong crossroad and joint point of Nguyen Chi Thanh street and De La Thanh Street. Overpass-bridge was built in Vong crossroad that bought the traffic jams not happen at this site. Consequently, the result of PAHs concentration in atmosphere reduced from 178 ng/m^3 to 22.89 ng/m^3. At the So crossroad (HN3) also the PAHs amounts in street air was rather reduced but they were more than 120 ng/m^3. At the joint point of Nguyen Chi Thanh street and De La Thanh street, the air concentration of PAHs deceased considerably in 2003 but at O Cho Dua Junction (HN15), PAHs amounts in air in 2003 were much higher than in the half beginning of 2002. So it needs to carry out continuous researches to explain this phenomenon more clearly.

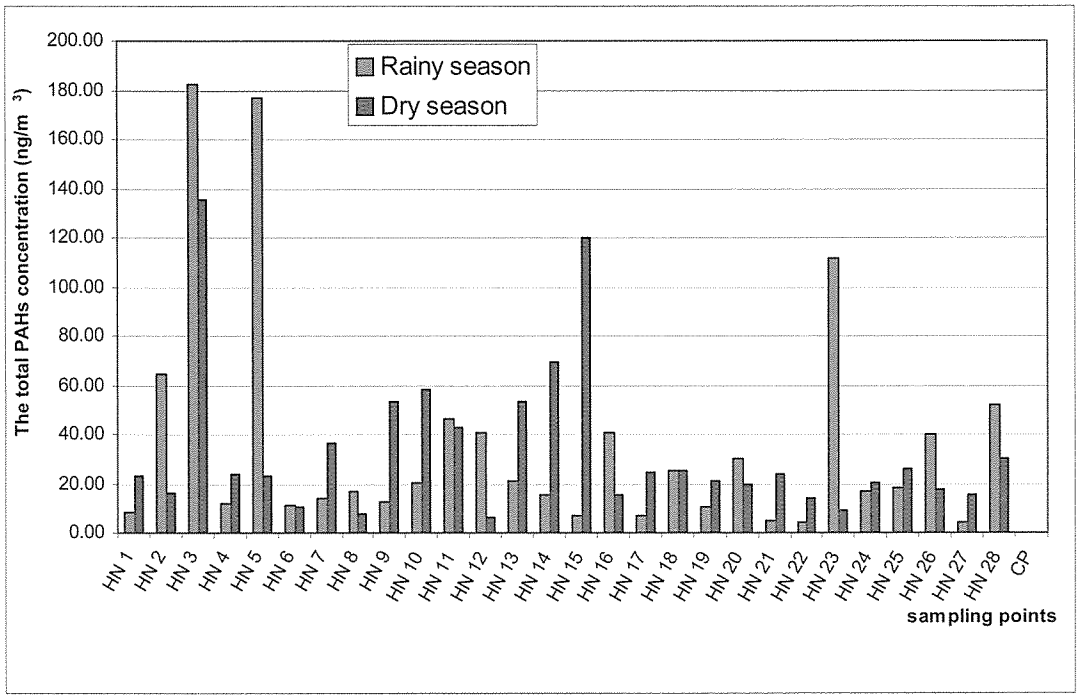


Figure 4.The total of PAHs concentration at 28 most important traffic joints in two seasons in the urban area of Hanoi

Almost observed traffic points the concentrations of PAHs in air environment were found in range of 20-60ng/m^3. At the joints of small streets, PAHs content in atmosphere were lower than 20ng/m^3. The difference became more obviously the PAHs amounts in air environment at all traffic joints of Hanoi in comparison those of Cuc Phuong forest where almost no PAH components could be detected in this reference sample at Cuc Phuong.

Distribution of PAHs

16 PAHs, which were studied, consisted of one 2-ring PAHs, five 3-ring PAHs, four 4-ring PAHs, four 5-ring PAHs, and two 6-ring PAHs. Among them, six compounds of PAHs such as benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and dibenzanthracenes are ranked as probable human carcinogens in the US-EPA Integrated Risk Information System (IRIS).

The average concentrations of the major PAHs at traffic joints were 31.75 ng/m^3 in dry season and 26.68 ng/m^3 in rainy season in Hanoi. Among 16 PAHs compounds were observed, the levels of 4-ring PAHs to 6-ring PAHs components were higher than the PAHs with a fewer

number of aromatic rings in molecular structures in both seasons. This proved that the polluted exhaust gases from motor vehicles used fuel of diesel and gasoline that had formed mainly 4-ring to 6-ring PAHs compounds. These groups were the most abundant PAHs in street air.
In the rainy season, the percentages of 2-3 aromatic ring PAHs were rather much higher than in dry season. Because of the diffusion ability of these compounds into air environment is stronger than their absorption on particle matter surface in dry season. Specially, the naphthalene amount in air was much larger in rainy season and its percentage was highest among 16 PAHs compound analysed.

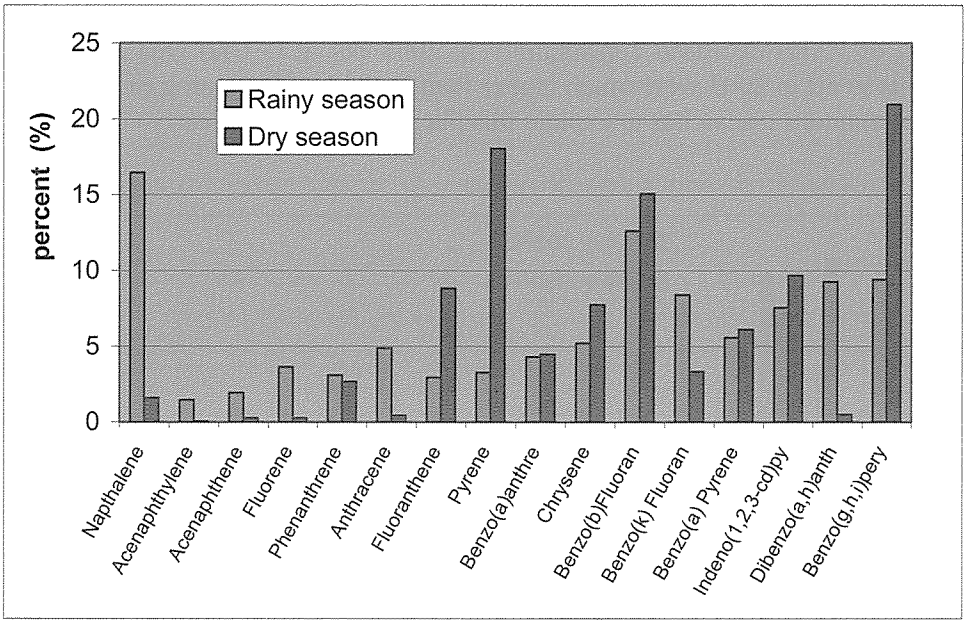


Figure 5. Percentages of each PAHs in the sum in two seasons

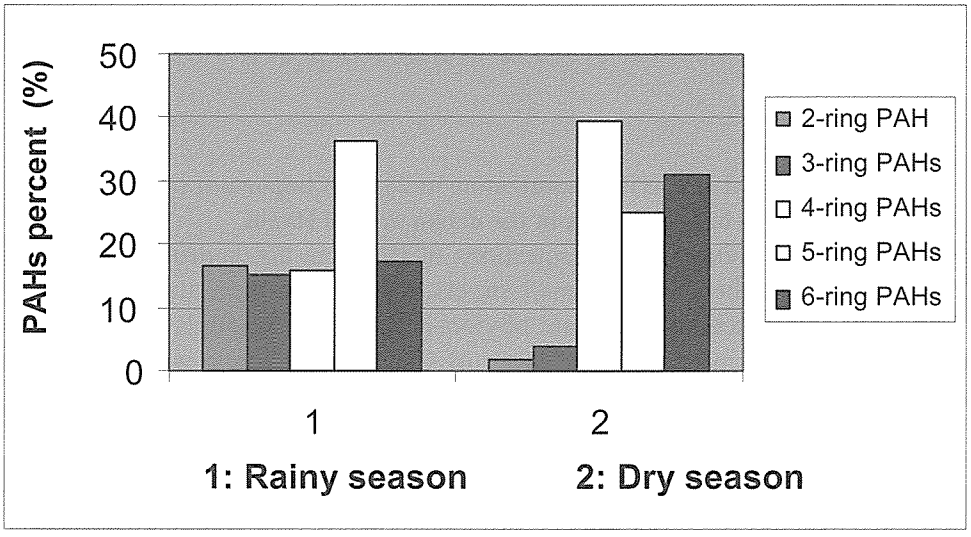


Figure 6: Percentage of 2-6 ring PAHs in two seasons

On the contrary, the levels of PAHs with large number of aromatic ring in structure (over 3 benzene rings) were dominant in the dry season and the Benzo(g,h,i)perylene, Pyrene and Benzo(b)fluoran were main compounds in 16 PAHs observed.

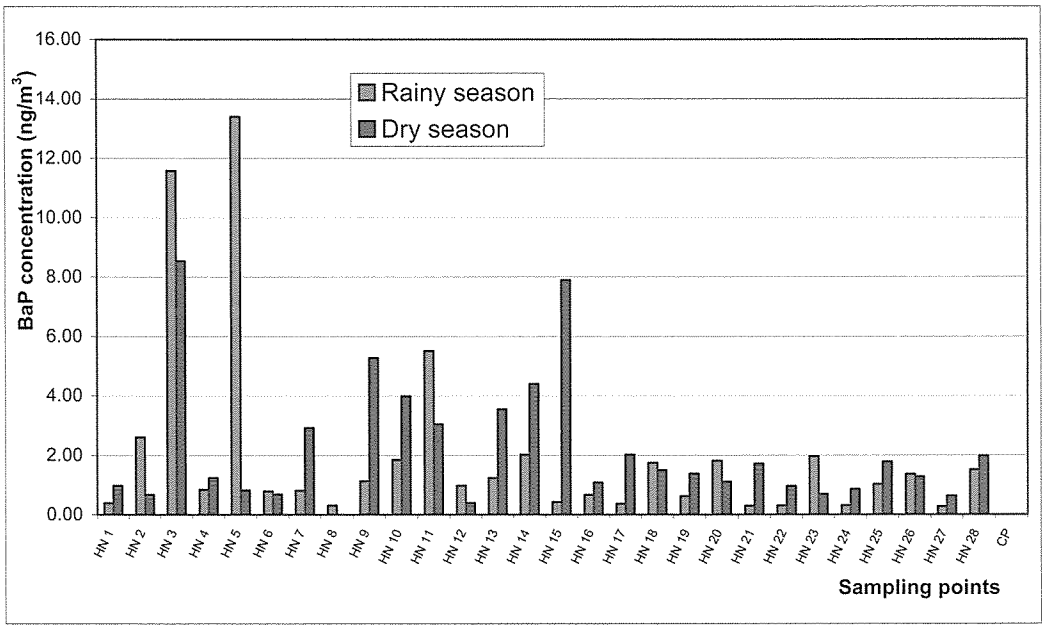


Figure 7.The BaP concentration at 28 most important traffic joints in two seasons in the urban area of Hanoi

Benzo (a) Pyrene, which is the most potential carcinogen in 16 PAHs compound, was found in average concentration 1.47 ng/m^3 in rainy season and 2.21 ng/m^3 in dry season. It is correspondent with high total PAHs amounts at the sampling points also obtained the high concentration of BaP at there. The highest amounts of BaP are found at So crossroad in both seasons 11.58 ng/m^3 in rainy season and 8.54 ng/m^3 in dry season.

CONCLUSIONS

The street dust samples were collected at the important traffic joints in Hanoi from April to July, 2002 and from December, 2002 to March, 2003 corresponding with rainy season and dry season in the Northern of Vietnam. These dust samples were measured 16 relevant PAHs components which are one of the abundant chemical groups caused from incomplete fuel combustion of motor vehicles. The concentrations of observed PAHs in street air environment were found in range of 3.34 - 182.8 ng/m^3 and 6.1 - 135.2 ng/m^3 in rainy season and dry season, respectively. In general, the average of PAHs total amounts in traffic air environment in dry season was higher than rainy season. The PAHs compounds with 4-6 aromatic rings in their molecular structures were predominant. Almost the traffic joints in Hanoi BaP concentrations were over the air ambient except limits of other countries in the world only 0.2-2ng/m^3 [12]. The next research will focus on seasonal fluctuation of PAHs also relation of sampling time during day and night in view a picture of atmospheric contaminant situation in Hanoi.

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INDEX

Table I. The air sampling sites at traffic joints in Hanoi city (from December, 2002 to March, 2003)

Sample sign	Sampling site	Sample sign	Sampling site
HN 1	Ha Dong Bridge	HN 16	Hue str. - Ham Long str.
HN 2	Ha Dong bus station	HN 17	Le Duan str.- Tran Hung §ao str.
HN 3	So Crossroads	HN 18	Cua Nam crossroads
HN 4	Petroleum station Truong Chinh-Ton That Tung str.	HN 19	Hoang Dieu Str.-Phan Dinh Phung str.
HN 5	Vong Crossroads	HN 20	Hoang Hoa Tham str.- Ngoc Ha str.
HN 6	Giai Phong Str. - Nguyen An Ninh str.	HN 21	Giang Vo Str. - Cat Linh Str.
HN 7	Truong Dinh Str.-Giai Phong Str.	HN 22	Lieu Giai Str.- Doi Can Str.
HN 8	Phap Van T-junction	HN 23	Nguyen Chi Thanh str.-De La Thanh str.
HN 9	Minh Khai Str.-Nguyen Khoai Str.	HN 24	Giay Bridge
HN 10	Tran Khat Tran Str. - Lo Duc Str. -Kim Nguu Str.	HN 25	Xuan Thuy Str.-Thang Long Str.
HN 11	Dai Co Viet Str.-Tran Khat Tran Str. - Hue Str.	HN 26	Hoang Quoc Viet Str.- Nam Thang Long Str.
HN 12	Lac Trung - Kim Nguu Str.	HN 27	Hoang Quoc Viet Str. - Buoi Str.
HN 13	Pham Ngoc Thach Str. - Chua Boc Str-Ton That Tung Str.	HN 28	Chui Bridge, Gia Lam
HN 14	Tay Son Str. - Chua Boc Str-Thai Ha Str.	HN 29	Au Co road - Nghi Tam Dist,
HN 15	O Cho Dua Crossroads	CP	Cuc Phuong Forest (Ninh Binh)