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Ambient Air Concentrations of Benzene, Toluene, Ethylbenzene and Xylene in Bangkok, Thailand during April-August in 2007

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ABSTRACT

Benzene, toluene, ethylbenzene and *m*-, *p*-, and *o*-xylene, the most influential aromatic volatile organic compounds (VOCs), were measured in Bangkok, Thailand, one of the most rapidly developing urban areas in Southern East Asia. The purpose of this study is to characterize the ambient air quality with respect to above mentioned aromatic compounds. The data were monitored in ten sites which cover roadside area, residential area and background area. Canister technique was used to obtain air sample at 24 hour interval per a month during April-August in 2007. GC/MS with three stage preconcentrator was used to analyze these samples. The average concentrations of benzene, toluene, ethylbenzene *m*-, *p*-xylene and *o*-xylene are 5.8, 36.1, 4.1, 11.0 and 3.7 μg/m^3, respectively. They were observed to be distributed in a log-normal form. Moreover, *o*-xylene and *m,p*-xylene exhibited a very good correlation (r=0.976). The slope of the regression equation between them was 3.07 which consisted with a previous reported value. The average ratio of toluene to benzene was 6.4 in April, May June and August. This value was comparable to the ones measured in other Asian cities. Two types of statistical analyses, cluster and factor analyses, were applied to the data in this study. Well characterization was made to understand the air quality of Bangkok area.

Key words: Volatile organic compounds, Bangkok, Log-normal distribution, Cluster analysis, Factor analysis

1. INTRODUCTION

Volatile organic compounds (VOCs) in the ambient air are of great concern because of their potential health impacts, formation of organic aerosols, photochemical smog production, and so on. Benzene, toluene, ethylbenzene and *m*-, *p*-, *o*-xylene are the most typical components of VOC pollution in air (Srivastava *et al.*, 2005a, b; Colon *et al.*, 2001; Chattopadhyay *et al.*, 1997). In short, it is essential to monitor the ambient air concentrations of these pollutants for the air quality improvement.

VOCs are emitted from a variety sources such as motor vehicle exhaust, gasoline evaporation, solvent usage, vegetative burning, and industrial emissions (Na *et al.*, 2003; Monod *et al.*, 2001; Rao *et al.*, 1997; Levin *et al.*, 1994). Of these sources, vehicle exhaust is known to be the most dominant VOC source in the atmosphere (Na, 2006; Thijesse *et al.*, 1999; Lawryk *et al.*, 1996; Fujita *et al.*, 1994). Emissions of benzene, toluene, ethylbenzene, xylene and so on from motor vehicle probably have the most serious effects on air quality. Among these, benzene is of particular concern since it is known to be a genotoxic carcinogen. In addition, VOCs also play a significant role in particulate formation and in the presence of NO_x, they react with OH radicals to form ozone (Parra *et al.*, 2006).

In Thailand, VOCs became a growing concern due to inappropriate use and management, leakage, improper transferring in production processes and some illegal waste disposal by industrial sector. Since some of VOCs are directly harmful to human health with respect to neurological effect, carcinogenicity and suspected human leukemogen, ambient VOCs concentration should be monitored. It is necessary to measure their concentrations to understand their behavior in the atmosphere.

For monitoring of VOCs in ambient air, two types of approached are available currently. One is on-line monitoring, while another is time-integrated measurements. Canister is one of time-integrated sampling well established for determination low level VOCs in

air at the parts per trillion , ppt (v), to parts per billion by volume, ppb (v), levels. Compared to the sorbent-based sampling method, the canister-based sampling method has many practical advantages, e.g. the collection of a whole air sample, sufficient sample volume for multiple analyses, simplicity of sampling procedure and applicability to a broad range of VOCs (Ochiai *et al.*, 2003).

The monitoring data of ambient VOC levels in developing countries are still limited (Zhao *et al.*, 2004; Cetin *et al.*, 2003; Gee *et al.*, 1998). In Thailand, governmental VOC measurement project started since summer of 2006. In this paper, we present our preliminary measurement data during April-August in 2007. It is considered that the characterization of VOC behaviors will provide basic information for making better countermeasures.

2. EXPERIMENTAL

2.1 Chemical and Preparation of Standard Gases

The standard mixtures of seventy-seven VOCs in high pressure cylinder (all in 1 ppm (v)) were purchased from Air Environmental, Inc. (USA). The internal standard mixtures containing bromochloromethane, 1,4-difluorobenzene and toluene-d8 at 1 ppm (v) was also purchased (Matheson Tri-gas, USA). The stock standards mixtures of seventy-seven VOCs were prepared at 20 ppb level by dilution into a 6 L silco-steel canister using an Entech 4600 dynamic dilution system (Entech Instrument Inc., Simi Valley, CA (USA)) with humidified nitrogen. Then the working standard in ppt level was prepared from this standard concentration by using pressure diluter. The internal standard mixtures at 2,000 ppt (v) is prepared with humidified nitrogen to be added to the calibration standards, blank and samples. To eliminate the adsorption of standard mixtures onto the interior surface of the sample path in the dilution system, a fused-silica-lined stainless steel tube (Silonite^{TM} Entech Instrument Inc.) was used for all sample path.

2.2 Apparatus and Materials

The 6 L silco-steel canisters were cleaned by 10-20 cycles of pressurization with humidified nitrogen (Ultra-high purity grade in gas cylinder) and evacuation

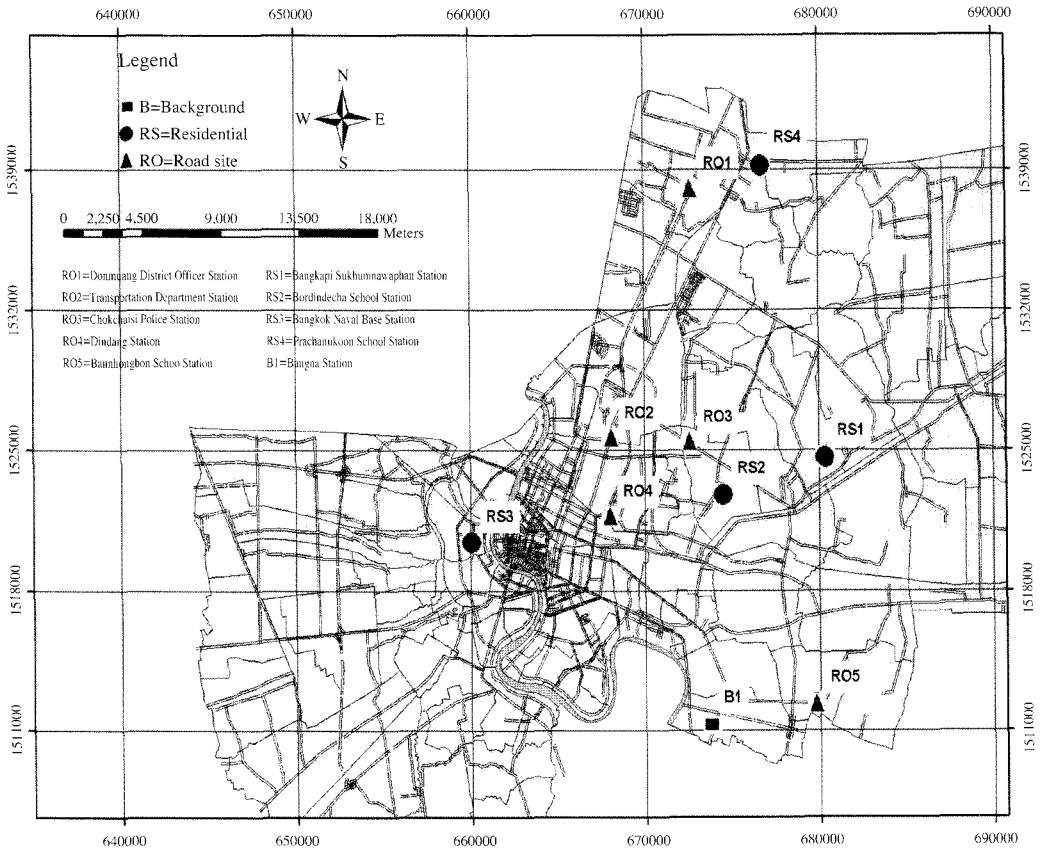

Fig. 1. Sampling sites in Bangkok area in Thailand (RO: Roadside area, RS: Residential, B: Background).

Table 1. Enviromental features of sampling sites in Bangkok area in Thialand.

Site number	Name of sampling station	Site character	UTM x, y coordinates	District located	Surrounding condition (traffic volume)
RO1	Donmuang District Officer	Roadside	672318, 1538355	Donmuang	Vipawadee road (12,600 cars/hr) and toll-way
RO2	Transportation Department	Roadside	667714, 1525914	Jatujak	Pahonyothin road (7,000 cars/hr)
RO3	Chokchaisi Police	Roadside	672180, 1525636	Ladpraow	Ladpraow road (5,100 cars/hr)
RO4	Dindang	Roadside	667609, 1522005	Dindang	Dindang road (6,800 cars/hr)
RO5	Bannhongbon School	Roadside	679577, 1522005	Prawes	Srinakarin road (5,500 cars/hr)
RS1	Bangkapi Sukhumnawaphan	Residential area	680340, 1524701	Bungkum	Low-rise and high-rise residential buildings
RS2	Bordindecha School	Residential area	674557, 1522832	Bangkapi	Schools and residential building
RS3	Bangkok Naval Base	Residential area	660128, 1520475	Bangkoknoi	On the grass field near a pond of navy base
RS4	Prachanukoon School	Residential area	676790, 1539354	Saimai	Residential area
B1	Bangna	Background	673673, 1511376	Bangna	A widely opened area

canister at about 100°C under high vacuum less than 50 mTorr using an Entech 3100A canister cleaning system (Entech Instrument Inc. USA). Cleaned canisters were filled with humidified nitrogen and analyzed to ensure that residue VOC content was less than the method detection limit. The evacuated cleaned canisters were used for standard preparation and sampling. The analysis based on three-stage preconcentration and gas chromatograph-mass spectrometer (GC-MS) was performed using Entech 7100A preconcentrator (Entech Instrument Inc. USA) and an Agilent 6890N GC with a 5973 inert mass selective detector (MSD). Temperature programming was set to cover from 0°C to 260°C. Liquid Nitrogen was used to cool the trap and the GC oven. The fused silica capillary column was used which its composed with 6% cyanopropyl-phenyl and 94% dimethyl polysiloxane (DB-624), 0.25 mm × 60 m × 1.4 mm.

2.3 Sampling

Prior to sampling, on site assemblies between a passive canister sampler and a canister was checked for leak. Air sample was drawn through a passive canister sampler with controlled flow rate at around 3.4 mL/min and introduced into a clean-evacuated silcosteel canister. VOC samples were taken on a 24-hr once a month basis from 10 sites in Bangkok area as shown in Fig. 1. The VOCs were collected during the time period of April to August in 2007.

2.4 Analytical Procedure

Prior to analysis, the pressure in the canisters was measured and pressurized with humidified nitrogen to about 200 kPa. The 100 mL of internal standards gas and the 400 mL of sample were initially trapped cryogenically on glass beads (Module 1, M1) at −150°C and then recovered by desorbing at 20°C to leave the water behind in the first trap, while slowly passing helium through to transfer VOCs to a second trap. The second cryotrap (Module 2, M2) containing Tenax was cooled to −10°C, which allows trapping of the complete range of VOCs, while flushing the CO_2 through the Tenax trap. Then the VOCs were back-flushed, while heating at 210°C to be further focused on an open-tubular focusing trap (Module 3, M3) at −160 °C. Heating of the focusing trap was performed by a rapidly injection on to the analytical column. The oven temperature was programmed at 0°C for 10 min, ramped at 5°C min^{-1} to 70°C, then ramped a second time at 15°C min^{-1} to 220°C and held for 5 min. The helium carrier gas was operated at a rate of 1.3 mL min^{-1}. The mass spectrometer was operated in the SIM mode.

2.5 Quality Assurance and Quality Control

The quality assurance and quality control (QA/QC) were performed through the following procedures: The blank check was made by being ensure that the blank sample did not contain any target VOCs over than 20 ppt (v). Multi-point calibration was performed using a five-point internal standard. The acceptance criteria of $r^2 \geq 0.99$ and percent relative standard deviation (RSD) of relative response factor (RRF) $\leq 20\%$ were used in the judgment of the calibration. Daily calibration was carried out using mid-level calibration standard. Duplicate sampling was made by using 10% of all sample number on their reproducibility. Method detection limit (MDL) and method quantification limit (MQL) were determined by making five replicate measurements of the standard gas at the lowest concentration among calibration standards to calculate the standard deviation for all target compounds. Table 2 shows QA/QC data in this study. They are considered to be acceptable for air quality measurement.

2.6 Environment of Sampling Sites

2.6.1 Roadside Stations

Bangkok is suffered from emissions of heavy traffics by motor vehicles as similar to big cities in other Asian

Table 2. QA/QC for BTEX analysis.

Compounds	Calibration		%D of Duplicate sampling	MDL ($\mu g/m^3$)	MQL ($\mu g/m^3$)
	r^2	%RSD RRF			
Benzene	0.997-1.000	3.6-13	0.50-9.3	0.008-0.052	0.026-0.173
Toluene	0.991-0.998	14-20	2.5-10	0.009-0.076	0.016-0.254
Ethylbenzene	0.997-1.000	4.9-20	0.90-11	0.006-0.021	0.021-0.069
m-, *p*-Xylene	0.990-0.998	8.4-20	1.8-19	0.002-0.018	0.005-0.059
o-Xylene	0.995-0.999	6.5-18	1.4-14	0.005-0.024	0.018-0.079

countries. In this study, the following five roadside sites were selected for the VOC sample collection. The detailed information of these sites is summarized in Table 1, including residential and background stations.

Donmuang District Officer Station: RO1

The former international airport of Thailand and domestic airport are located to opposite side of this sampling site. The population in Donmuang district is about 158,000 persons. In about 500 meters radius, there are two car garages and resident buildings.

Transportation Department Station: RO2

The sampling site is adjacent to the junction of Pahonyothin road and close to car parking. The population in Jatujak district is about 170,000 persons. Open markets, an engine garage school and residential buildings are located in about 500 meters radius.

Chokchaisi Police Station: RO3

There are low-rise and high-rise residential buildings, one gasoline station, food market and other commercial buildings in about 500 meters radius. The population in Ladpraow district is about 116,000 persons.

Dindang Station: RO4

In about 500 meters radius, there are 3 gasoline stations, commercial buildings, low-rise and high-rise residential buildings, mobile meat grills, small restaurants and waste water treatment facility. The population in Dindang district is about 147,000 persons.

Bannhongbon School Station: RO5

The site is situated at the 2nd floor of Bannhongbon School. There are schools, commercial buildings, residential buildings, one gasoline station, three car garages and mobile meat grills In about 500 meters radius. The population in Prawes district is about 139,000 persons.

2.6.2 Residential Area Stations

The following four sites are selected to be as representatives for the residential area in Bangkok. These sites are considered not to be directly influenced by heavy traffic roads.

Bangkapi Sukhumnawaphan School Station: RS1

There are low-rise and high-rise residential buildings and one car garage in about 500 meter radius. The population in Bungkum is about 138,000 persons.

Bordindecha School Station: RS2

There are schools, residential building, mobile meat grills, two car garages and one furniture factory in about 500 meter radius. The population in Bangkapi district about 148,000 persons.

Bangkok Naval Base Station: RS3

There are densely residential villages, a hospital, a car garage and a gasoline station in about 500 meters radius. The population in Bangkoknoi district is about 136,000 persons.

Prachanukoon School Station: RS4

There are densely residential villages, small shops, mobile meat grills and a car garage in about 500 meter radius. The population in Saimai district is about 162,000 persons.

2.6.3 Background Station

We selected one site as a background station. However, it is not a generally meaning background, but only less polluted compared with above mentioned stations at roadside and residential area.

Bangna Station: B1

This sampling site is located to boundary zone between urban area and industry area. There are Meteorological Department, residential offices, golf court, two gasoline stations and a temple n about 500 meter radius. The population in Bangna district is about 102,000 persons.

2.7 Statistical Analyses

The cluster (Ward, 1963) and factor (Hsieh *et al.*, 2006) analyses were applied to characterize the impact of relevant sources of VOCs at 10 sites in Bangkok. This was achieved by the use of the software package of STATISTICA version 5.0, which was supplied by Statsoft Co., Ltd.

In cluster analysis, the method to minimize the sum of squares of any two clusters that can be formed at

each step was applied. The multivariate method of factor analysis was performed by orthogonal transformation with Varimax rotation. In short, in the extraction of principal components, a variance maximizing rotation of the original variable space was applied. The retention of principal component was determined on the criteria that eigenvalues are greater than one.

In factor analysis, we can also estimate the actual values of individual observations for respective factors, which are called factor scores. In this research, characteristics of sampling sites were argued in this viewpoint.

3. RESULTS AND DISCUSSION

3.1 Characteristics of Distribution of VOC Concentrations

Fig. 2(a)-(e) show the frequency distributions of selected VOC concentrations in Bangkok area. All the data obtained were compiled in number of sample appearance by every specified interval.

Benzene concentrations as shown in Fig. 2(a) ranged from 1.2 μg/m^3 to 19.8 μg/m^3. The average concentration was 5.8 μg/m^3 with a maximum frequency of the range of 2-4 μg/m^3. The value is considered to be high because the environmental quality standard in Thailand is 1.7 μg/m^3. The data in this paper were comparable with other urban cities i.e., 2.0-6.0 μg/m^3 in Texas (Reiss, 2006), 2.0-4.0 μg/m^3 in Hong Kong (Lee *et al.*, 2002), 3.2 μg/m^3 in Seoul (Na *et al.*, 2001), 4.6 μg/m^3 in Sao Paulo (Colon *et al.*, 2001), 6.9 μg/m^3 in Berlin (Monod *et al.*, 2001) and 9.6 μg/m^3 in Algeria (Rabah *et al.*, 2006).

Fig. 2(b) shows the frequency distribution of toluene concentrations in Bangkok area similarly to the above with respect to benzene. Toluene was the most abundant atmospheric aromatic hydrocarbon, followed by *m,p*-xylene and benzene. In this case, the concentration interval was set to be 10 μg/m^3 because toluene concentrations were at higher levels compared with other VOCs. They ranged from 5.0 μg/m^3 to 99.7 μg/m^3. The average concentration was 36.1 μg/m^3. Maximum frequency fell in the range of 30-40 μg/m^3. The values are considered to be generally considerable high in the comparison of previous reported data in other urban cities: 4-36 μg/m^3 in Hong Kong (Lee *et al.*, 2002), 27 μg/m^3 in Taiwan (Hsieh *et al.*, 2003), 28 μg/m^3 in Sao Paulo (Gee *et al.*, 1998), 30 μg/m^3 in Santiago (Gee *et al.*, 1998), 31 μg/m^3 in Hamburg (Bruckmann *et al.*, 1988), 34 μg/m^3 in Sydney (Nelson *et al.*, 1982), 41 μg/m^3 in Vienna (Lanzerstorfer *et al.*, 1990), 54 μg/m^3 in Athens (Moschonas *et al.*, 1996), 55 μg/m^3 in Atlanta (NRC, 1991) and 39.2 μg/m^3 in Algeria (Rabah *et al.*, 2006).

Higher concentrations of toluene might result from nearby construction work (such as painting) and evaporation from car painting plants and industries during sampling period.

Fig. 2(c) shows the frequency distribution of ethylbenzene concentrations in Bangkok area, similarly. In this case, the concentration interval is set to be 2 μg/m^3. They ranged from 0.6 μg/m^3 to 13.1 μg/m^3. The average concentration was 4.1 μg/m^3. Maximum frequency fell in the range of 2-4 μg/m^3. They seem to be at a little bit of higher levels compared with ones in other urban cities i.e., 2.0-4.0 μg/m^3 Hong Kong (Lee *et al.*, 2002), 2.6 μg/m^3 in Chicago (Aronian *et al.*, 1989), 2.8 μg/m^3 in Berlin (Monod *et al.*, 2001), 6.0 μg/m^3 in Sao Paulo (Gee *et al.*, 1998), 6.5 μg/m^3 in Santiago (Gee *et al.*, 1998) and 6.3 μg/m^3 in Algeria (Rabah *et al.*, 2006).

Fig. 2(d) shows the frequency distribution of *m,p*-xylene concentrations in Bangkok area, in similarly above data. The concentration interval is set to be 10 μg/m^3 because *m,p*-xylene concentrations were at higher levels. They ranged from 1.5 μg/m^3 to 57.6 μg/m^3. The average concentration was 11.0 μg/m^3. Maximum frequency fell in the range of 0-10 μg/m^3. In the comparison of previous reported data, the data were at a comparable to higher levels: 3.0-15 μg/m^3 in Hong Kong (Lee *et al.*, 2002), 6.5 μg/m^3 Taiwan (Hsieh *et al.*, 2003), 6.5 μg/m^3 in Chicago (Aronian *et al.*, 1989), and 7.5 μg/m^3 in Berlin (Monod *et al.*, 2001).

Fig. 2(e) shows the frequency distribution of *o*-xylene concentrations, one of isomers of *m,p*-xylene, in Bangkok area. The concentration interval is set to be 2 μg/m^3 because *o*-xylene concentrations were at lower levels compared with ones of *m,p*-xylene. They ranged from 0.6 μg/m^3 to 18.3 μg/m^3. The average concentration was 3.7 μg/m^3. Maximum frequency fell in the range of 2-4 μg/m^3. They were at a similar levels in other urban cities i.e., 1.5-3.0 μg/m^3 in Hong Kong (Lee *et al.*, 2002), 2.2 μg/m^3 in Bombay (Mohan Rao *et al.*, 1997), 2.9 μg/m^3 in Berlin (Monod *et al.*, 2001), and 3.5 μg/m^3 in Seoul (Na *et al.*, 2001).

All the distributions shown in Fig. 2(a)-(e) seem to be not in a form of a simple normal distribution, but almost in a logarithmic normal distribution. Basically air pollutants are apt to be distributed in the form of logarithmic normal distribution, not symmetrically in a bell shape form. It is generally called as Larsen distribution, in which relatively low concentrations appear more frequently than higher concentrations (Seinfeld *et al.*, 1998). In this study, we found that the appearance frequencies of selected VOC concentrations in Bangkok area could be considered in the form of logarithmic normal distribution under the considera-

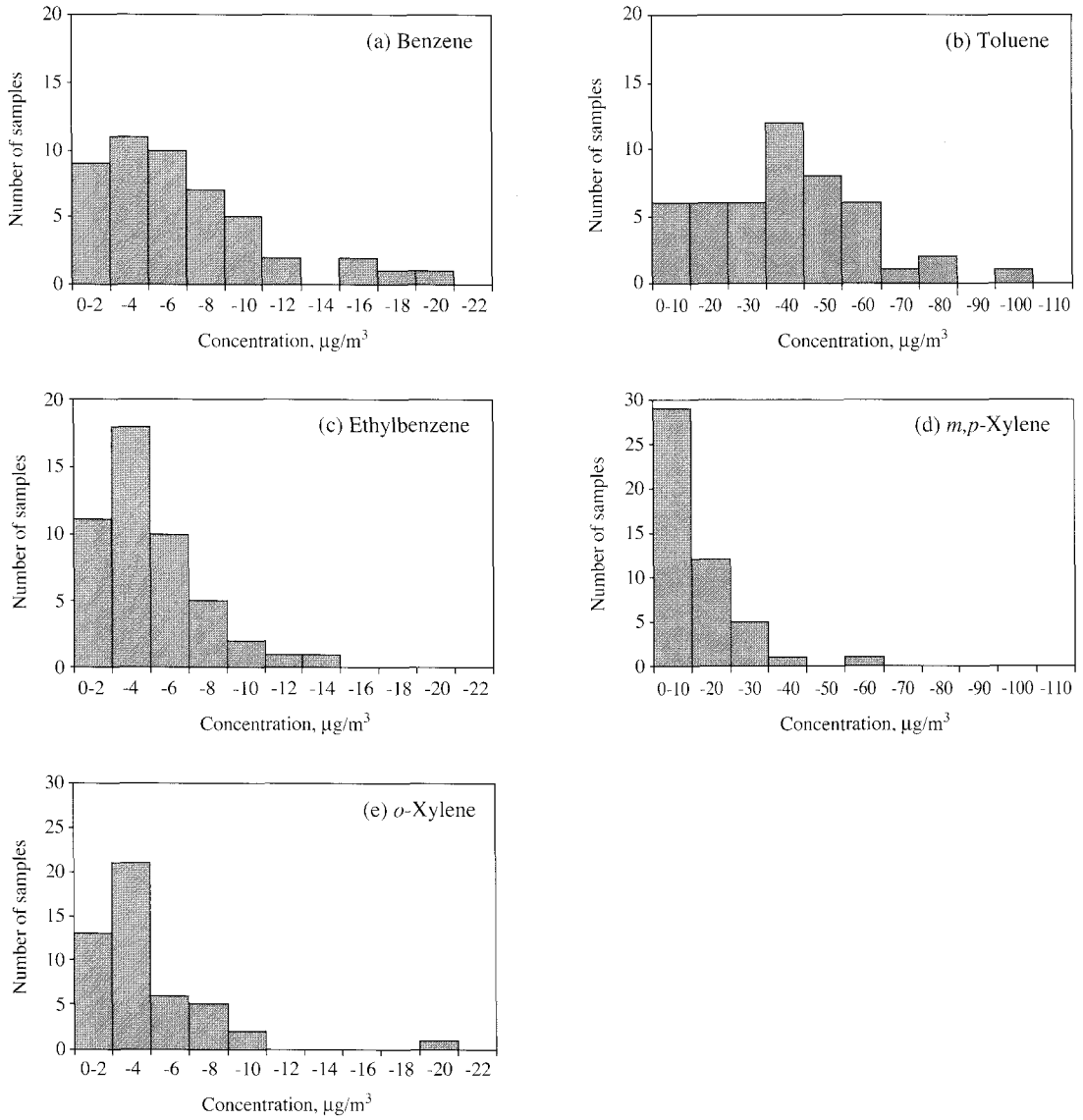

Fig. 2. Appearance frequency of selected VOCs in Bangkok area in Thailand. (a) Benzene (Average=5.8 μg/m^3) (b) Toluene (Average=36.1 μg/m^3) (c) Ethylbenzene (Average=4.1 μg/m^3) (d) *m,p*-Xylene (Average=11.0 μg/m^3) (e) *o*-Xylene (Average= 3.68 μg/m^3), (n=48).

tion that they have a common comprehensive characteristic. Ohura *et al.* (2006) gave a similar comment that most of VOCs detected in Shizuoka, Japan were distributed log-normally although the data were not shown in their paper.

In general, ambient air concentration data have been often shown as μ±SD (mean and standard deviation). However we may conclude the expression is not appropriate because the data are not always distributed in the form of normal distribution. The following comment is supporting the above discussion: Kim *et al.* (2002) reported that they observed some large values as outlier in their measurement BTEX in Seoul and showed both mean and median (or mode) value together rather than relying on the mean and SD value.

3.2 Correlation of between Selected VOCs

Table 4 shows the slopes and correlation coefficients between variations in the ambient air of selected VOCs on the basis of the discussion in previous papers (Monod *et al.*, 2000; Nelson and Quigley, 1983). The monitored data were examined by site character as described in the section of environment of sampling sites.

There are many factors which influence the VOC characteristics in Bangkok, Thailand. We will give

some possible interpretation to our limited results at the present time. Further it is necessary for us to obtain more data and do more intensive measurements in order to understand their profiles clearly.

3.2.1 The Relation between Xylenes and Ethylbenzene

Nelson and Quigley (1983) reported that *m,p*-xylene to ethylbenzene ratio was constant throughout different sources such as vehicle exhaust, solvent petrol and fuel evaporation. They found that a *m,p*-xylene to ethylbenzene ratio was about 3 at 50 percentile value in the frequency distribution observed in Sydney air taken at 0600 h. Moreover, Monod *et al.* (2000) summarized this ratio calculated from more data found in the literature and their experimental results. They concluded that the ratios in different sources samples were relatively constant ranging 2.8 to 4.6 and the overall average value was 3.5 ± 0.5.

In this study, the ratios at roadside, residential and background sites are 1.96, 3.17 and 1.86, respectively. Their correlation coefficients are considered to be enough high. These values are considered to be acceptable. On the other hand, according to previous discussions (Monod *et al.*, 2000; Nelson and Quigley, 1983), the xylenes and ethylbenzene are emitted by the same major sources, but decay at different rates from OH-oxidation in the atmosphere. Therefore, the ratio has been considered to be a tool to investigate the photochemical age of an urban plume. Moreover, it is also pointed out that the difference in oxidation rate between *m*-xylene and ethylbenzene is larger than the one of *p*-xylene and ethylbenzene (Atkinson *et al.*, 1979) although they are not separately determined in this study. From these stand points, our results are not easily understandable because the ratio at roadside sites are lower than the one at residential sites.

Moreover, the relation between *o*-xylene to ethylbenzene ratio was well correlated as shown in Table 4. Hsieh *et al.* (2006) discussed the ratio of xylenes (*m,p*-xylene to ethylbenzene+*o*-xylene) to ethylbenzene in the measurement in Taiwan. They concluded the ratio was a good index to evaluate the air quality.

In summarization of above results, three xylenes and ethylbenzene must be emitted by same sources in all the areas investigated in this study, which may be mostly vehicles.

3.2.2 The Relation between Toluene and Ethylbenzene

Toluene and ethylbenzene are reported to be emitted by both fuel evaporation and combustion processes (Sigsby *et al.*, 1987). Moreover, toluene is widely used in many ways as industrial material. It is shown that slopes are larger than the ones with respect to xylenes and the correlations are not so high in roadside and residential areas in the Table 4. The atmospheric life time of ethylbenzene towards OH radicals is comparable to that of toluene (Atkinson *et al.*, 1979). However, the above results are obtained in this study. This may be the consequence of other sources of toluene in Bangkok area, such as architectural surface coating, graphic arts, industrial solvents and chemical feedstock (Aronian *et al.*, 1989).

3.2.3 The Relation between Benzene and Ethylbenzene

The correlation coefficient between benzene and ethylbenzene was lower and the slope was small compared with the toluene case. This is in part because their atmospheric life time towards OH radicals are different (Atkinson *et al.*, 1979). Ho *et al.* (2004) reported that benzene in the tunnel showed relatively low correlation with ethylbenzene whereas the correlations between benzene/xylene and xylene/ethylbenzene are very high. Although they considered that the major emission of benzene was from vehicular exhaust, their results suggest the complicated behavior

Table 3. Factor analysis results for selected VOCs in Bangkok area in Thailand.

	Factor loading	
	Factor 2	Factor 1
Benzene	0.274	0.948
Toluene	0.727	0.508
Ethylbenzene	0.953	0.164
m,p-Xylene	0.834	0.511
o-Xylene	0.785	0.590
Eingenvalue	2.82	1.79
Contribution ratio	0.564	0.359

Table 4. Correlation between selected VOCs by site character in Bangkok area in Thailand.

Site character	*m,p*-Xylene/ Ethylbenzene		*o*-Xylene/ Ethylbenzene		Toluene/ Ethylbenzene		Benzene/ Ethylbenzene		Toluene/ Benzene		n
	Slope	R	Slope	R	Slope	R	Slope	R	Slope	R	
Roadside	1.96	0.898	0.718	0.796	7.80	0.318	1.03	0.359	6.50	0.394	20
Residential area	3.17	0.856	1.04	0.864	8.36	0.602	1.42	0.389	4.73	0.484	25
Background	1.86	0.917	0.457	0.963	3.83	0.954	0.235	0.271	12.8	0.333	3

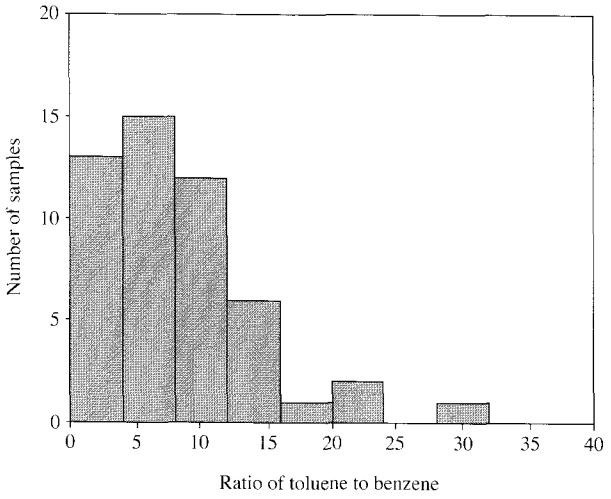

Fig. 3. The frequency distribution of the ratio of toluene to benzene in Bangkok area in Thailand (Ratio interval=4, Average=8.4, n=48).

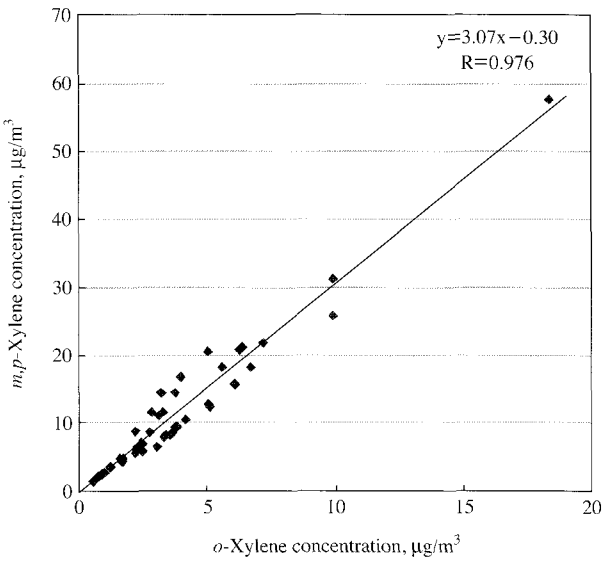

Fig. 4. The relation between *o*-xylene and *m,p*-xylene in Bangkok area in Thailand (n=48).

of benzene in the ambient air. These results might relate to our monitoring ones which seem to be not a simple relation between benzene and ethylbenzene.

3.2.4 The Relation between Toluene and Benzene

Previous papers have reported the ratio of toluene to benzene (T/B) (Hsieh *et al.*, 2006; Ho *et al.*, 2004; Lee *et al.*, 2002; Mond *et al.*, 2001). Lee *et al.* (2002) suggested that T/B ratio increases with increasing traffic volume, industrial emissions and other urban sources in denser areas.

In addition to Table 4, Fig. 3 shows the frequency distribution of the ratio of toluene to benzene in Bangkok area. There is a character between these components that benzene is the least photochemical reactive and toluene is the most affluent component among BTEX (Monod *et al.*, 2001; Atkinson *et al.*, 1979). In this case, the concentration width was set to be 4 times. The average ratio was 8.4. Maximum frequency fell in the range of 4-8 times.

The ratio was observed exceptionally as high as between 10.0 and 31.3 (average=15.9) in June. The high T/B might indicate that large additional sources of toluene are emitted from some industries, or alternatively that auxiliary fuels used differ significantly. Excluding the data in June, the average was 6.4 in this study. In our previous paper (Laowagul *et al.*, in press), it was observed that the ratios ranged between 4-9 with the average of 5.7 at around Pathumwan junction where was one of the most heavy traffic area in Bangkok, Thailand in April-June in 2003.

In Hong Kong, the range of T/B was around 5 (Lee *et al.*, 2002) and 3-8 in winter and 5-14 in summer (Ho *et al.*, 2004). Previously, high values of T/B were observed in Asian cities, such as Manila (T/B=10), Bangkok (T/B=10), Korea (T/B=6) (Na and Kim, 2001; Gee and Sollars, 1998). However, values of around 2-3 were reported in many cities such as Algeria (Kerbachi *et al.*, 2006), Cairo (Khoder *et al.*, 2007) and southern Taiwan (Hsieh *et al.*, 2006).

The ratio in this study may be concluded to be fairly high. The large additional sources of toluene than traffic sources must give intensive influences to the air quality in Bangkok area.

3.3 Correlation of *o*-xylene and *m,p*-xylene

The relation between *o*-xylene and *m,p*-xylene is sepecially paid attention in this study. Although Monod *et al.* (2001) showed the very distinguishable results with respect to them, no discussions have been made directly on this issue. Monod *et al.* (2001) reported that the correlations of *m*-xylene/*p*-xylene and *m*-xylene/*o*-xylene were very well for all the samples in urban air, traffic air and liquid fuel in places including Paris, Santiago, Hongkong, Bangkok and Shenzen. Moreover, the ratios are constant for all the samples. That is, concentration ratios of *m*-xylene/*p*-xylene and *m*-xylene/*o*-xylene are 2.33 and 1.84 respectively. They did not show the ratio of *o*-xylene and *m,p*-xylene directly. It can be easily calculated to be 3.12

Fig. 4 shows the relation between *o*-xylene and *m,p*-xylene in Bangkok area. They seem to have very good correlation (r=0.976). The intercept of the regression line is negligibly small. The slope of our

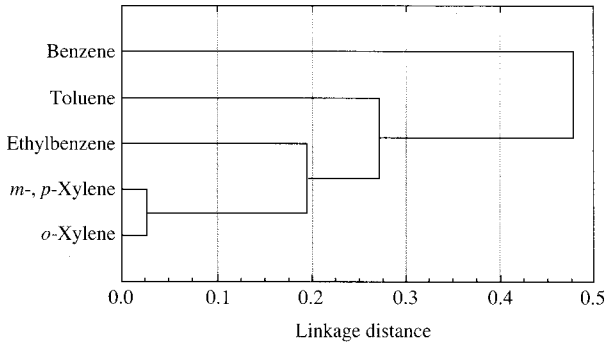

Fig. 5. Cluster analysis of selected VOCs in Bangkok area in Thailand.

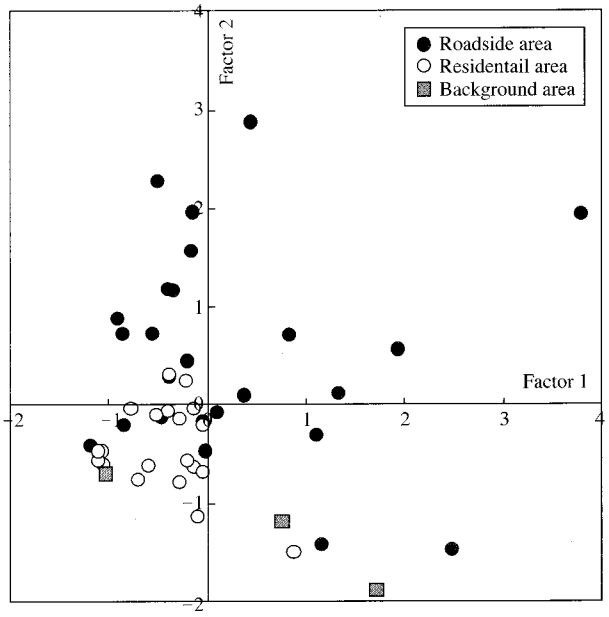

Fig. 6. Factor scores of factor analysis through measurements of selected VOCs in Bangkok area in Thailand.

evaluation as mentioned above is very close to the one by Monod *et al.* (2001). Thus, the ratio of *o*-xylene and *m,p*-xylene can be considered almost constant in all the Bangkok area although the concentration levels are different depending on site and date. The ratio is evaluated to be about 3.07 in this study. Our result is close to the measurement in Hong Kong (Guo *et al.*, 2007) in which the ratio was about 3.13 (r= 0.999).

On the other hand, Monod *et al.* (2001) reported that the correlations of *m*-xylene/*p*-xylene and *m*-xylene/*o*-xylene were very well for all the samples in urban air, traffic air and liquid fuel in places including Paris, Santiago, Hongkong, Bangkok and Shenzen. Moreover, the ratios are constant for all the samples. That is, concentration ratios of *m*-xylene/*p*-xylene and *m*-xylene/*o*-xylene are 2.33 and 1.84 respectively. They did not show the ratio of *o*-xylene and *m,p*-xylene directly. It can be easily calculated to be 3.12 which is very close to our evaluation as mentioned above.

The reason will be derived from the fact that *o*-xylene and *m,p*-xylene are isomers. Their boiling points are close as being between 138.4-144.5°C (Monod *et al.*, 2001). Therefore they will evaporate simultaneously in the environment. Moreover it is possible for these compounds to behave similarly in the combustion processes because their chemical properties may be similar as isomers.

3.4 Statistical Analysis

Fig. 5 shows the dendrogram as classification of BTEX by cluster analysis. It is an exploratory data analysis tool which aims at sorting different objects into groups in a way. In this study, Ward's method (Ward, 1963) was applied using correlation coefficients between components of BTEX.

The result implies that *m*-, *p*-xylene and *o*-xylene have a very close relation and ethylbenzene has next familiarity with xylene isomer group. Then toluene joins in the xylene and ethylbenzene family in the dendrogram. Therefore, it is considered that those spcies would be mostly derived from same kinds of sources. Benzene shows an independent characteristic. Although it is also released from the processes in exhaust gas, evaporation and industries in general, some specified sources might give strong influences to air quality in Bangkok area.

On the other hand, Table 1 shows the results of factor analysis with respect to selected VOCs in Bangkok area. Factor analytical techniques are to reduce the number of variables and to obtain extracted factors which could explain the common variance of these VOCs as Hsieh *et al.* (2006) commented. Two main factors, Factor 1 and Factor 2, were extracted. Eigenvalues of Factor 1 and Factor 2 are 2.82 and 1.79, respectively. The contribution ratio of these two factors is calculated to be 92.3%.

It is possible to interpret the relation between sources and factors (Guo *et al.*, 2007; Hsieh *et al.*, 2006). Sources of VOCs may be nominated as follows: Vehicle emission, fuel evaporation, combustion source, solvent usage, oil/coal burning, industrial source and so on (Guo *et al.*, 2007). In Factor 1, factor loadings of ethylbenzene and xylenes are very large and factor loading of toluene follows. Vehicle emission may be mainly ascribed to Factor 1. On the other hand, in Factor 2, factor loading of benzene is noticed to be the

largest. Factor loadings of xylenes are next large. Then Factor 2 is considered to represent mainly the industrial sources. This interpretation is partially similar to the conclusion by Hsieh *et al.* (2006), who applied factor analysis to VOC measurements in Taiwan and showed that toluene and benzene were ascribed to different factors.

Fig. 6 shows the factor scores by sampling site on a plain of Factor 1 (x-axis) and Factor 2 (y-axis). Sampling sites are categorized into roadside area, residential area and background area. Air pollution levels at the background area are apparently low compared with other areas. Two gasoline stations were located to northern direction from the site. No direct influences were given from them because dominant wind directions were south to southwest during the sampling periods. In fact, their points exist in the area of right hand and lower side of the plain which are shown in square. It is a nominal background where is less polluted than sites in other categories.

Next data group are the ones monitored in the residential area which are shown in open circle. They are scattered at the positions in the plain which are more polluted than the ones of background area. Moreover, data in the roadside area are widely scattered at more polluted positions in the plain which are shown in closed circle. Some of them were strongly influenced by Factor 1 and others are also influenced by Factor 2.

We can conclude through the above discussion that statistical analysis is useful to characterize the air quality of Bangkok area. However, data are still limited in this study. Further detailed data are necessary to understand the characteristics of the air pollution more concisely.

4. CONCLUSION

In this study, characterization of VOCs, focusing benzene, toluene, ethylbenzene and *m*-, *p*-, *o*-xylene, was carried out in Bangkok, Thailand. The data were monitored in ten sites which cover roadside area, residential area and background area during April-August in 2007. The sampling was conducted on 24 hours basis once a month by canister system. The analysis was done by GC/MS with a preconcentrator system. Results were summarized as follows:

(1) The average concentrations of benzene, toluene, ethylbenzene *m*-, *p*-xylene and *o*-xylene are 5.8 $\mu g/m^3$ (ranged from 1.2 $\mu g/m^3$ to 19.8 $\mu g/m^3$), 36.1 $\mu g/m^3$ (ranged from 5.0 $\mu g/m^3$ to 99.7 $\mu g/m^3$), 4.1 $\mu g/m^3$ (ranged from 0.6 $\mu g/m^3$ to 13.1 $\mu g/m^3$), 11.0 $\mu g/m^3$ (ranged from 1.5 $\mu g/m^3$ to 57.6 $\mu g/m^3$) and 3.7 $\mu g/m^3$ (ranged from 1.5 $\mu g/m^3$ to 57.6 $\mu g/m^3$), respectively. They were observed to be distributed almost in a log-normal form. Moreover, those levels are comparable to urban areas in developing countries.

(2) The relation between *o*-xylene and *m,p*-xylene had very good correlation (r=0.976). The slope was 3.07 which consisted with a previous reported value of 3.12 in many sites in developed and developing countries.

(3) The ratio of benzene to toluene was 6.4 excluding data in July in which toluene concentrations were very high. This value was considered to be at comparable to fairly higher levels compared with the ones in other Asian cities. The additional other sources of toluene than traffic sources must give intensive influences to the air quality in Bangkok area.

(4) Cluster and factor analyses, were applied to the data in this study. Well characterization was made to understand the air quality of Bangkok area. It was discussed that Factor 1 and Factor 2 in factor analysis were ascribed possibly to vehicle emission and industrial sources, respectively.

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