Characterization of Benzene, Toluene, Ethylbenzene, and Xylene Concentrations in the Ambient Atmosphere of Tokyo, Japan

Wanna LAOWAGUL1), Kunio YOSHIZUMI2)
1)Environmental Research and Training Center:
Tambon Klong 5, Amphoe Klong Luang, Pathumthani 12120, Thailand
2)Kyoritsu Women’s University: 2-2-1 Hitotsubashi, Chiyoda-ku, Tokyo 101-8437, Japan

Abstract

Extensive volatile organic carbons (VOCs) data for a 12-month measurement period, which were collected by the Bureau of the Environment, Tokyo Metropolitan Government, are examined in this study. Behavior of benzene, toluene, ethylbenzene, and xylene was discussed, which were monitored at two specified sampling locations, roadside (Hachimanyama) and residential area (Shirogane) in 2001. The monthly variations of these compounds showed two peaks in June and November. The high concentrations in June were considered to be derived from the unburned and evaporated components of fuel due to raised ambient temperature. On the other hand, atmospheric conditions in Tokyo are generally very stable in November. These conditions would result in the peak in November in monthly variations. The concentrations of benzene and xylene were higher at the roadside than that at residential site. These readings were considered to be strongly influenced by vehicle emissions. The difference between concentrations at the both sites was small with respect to toluene and ethylbenzene. Their sources may be not only vehicles but also some stationary sources. The ratios between m,p-xylene to o-xylene were observed to be constant throughout the year with the exception of June, July, and August only at the residential site.

Keywords: VOCs, ambient air, Tokyo, monthly variation, roadside, residential area

I. Introduction

An increased awareness of volatile organic carbons (VOCs) has raised concerns that their release may prove to be a health hazard. The adverse effects on health from exposure to air toxins and hazardous air pollutants have been discussed in previous articles [1-6]. A number of VOCs have been identified as important risk factors in urban environments [7-26].

There are many anthropogenic sources that emit a variety of VOCs to the atmosphere in urban areas. Once entering the atmosphere, most VOCs react rapidly with hydroxyl radicals and nitrogen oxides in sunlight to form ozone, other oxidants, secondary VOCs, and particulate matter [27-29].

The abundance and specification of VOCs in the ambient environment greatly affects atmospheric chemical reactions. On the other hand, many VOCs in urban air are toxic, and some are well known carcinogens [30-34]. In addition, the secondary VOCs generated in the photochemical reaction are often more hazardous to human health and environmental quality [35-37].

Therefore, to evaluate the relative importance of various VOCs in ozone production, and to reduce human exposure to toxic VOCs in the atmosphere, detailed VOCs speciation and quantification in urban atmospheres is necessary.

A large number of research papers on these compounds in urban areas have been published [7-26]; however, detailed information required for understanding their behavior is still limited, because of the complexity of influences on their characteristics. VOC behavior depends on variations in such
factors as meteorological conditions, ambient secondary reaction, the relative position of the subject and source, and vehicle traffic volume.

Extensive VOCs data have been collected in Tokyo and made available for public use by the Bureau of the Environment, Tokyo Metropolitan Government [38]. In this study, data from a 12-month measurement period for selected VOCs, which was conducted at two specified sampling locations between January 1 and December 31 in 2001, are examined. We mainly focus on interpreting monthly trends of benzene, toluene, ethylbenzene, and xylene (BTEX) and the ratios between them in Tokyo. That is, their behaviors are characterized to obtain a basic knowledge needed to control the air quality.

II. Experimental

1. Air monitoring and sampling sites

Air monitoring data for BTEX were obtained from Air Quality Monitoring Information of the Tokyo Metropolitan Government. These data were collected at two sites, Hachimanyama and Shirogane, in Tokyo (Fig. 1) in 2001.

The Hachimanyama site was on the roadside at a distance of 3.5 m from Circular Route No. 8, one of the busiest roads in Tokyo. We expected that the air quality at the site would be directly influenced by vehicle exhaust. In contrast, the Shirogane site is located in a residential area. It is 100 m away from Kasuga Street, and has only a moderate volume of traffic. We considered that the air quality at this site would not be directly influenced by vehicle exhaust emissions.

2. Analytical procedure

At each sampling site, air samples were taken every hour from a height of about 5 m, via an inlet made of a glass cylinder. The contents of each 600 mL of air sample were trapped cryogenically on an absorbent matrix (Carbotrap B + Carbosieve) at −20°C for 10 min, using a Shimazu TD-1 preconcentrator. During this process, water was removed by a permeation technique. The VOC sample was then subjected to GC-MS (Shimazu GC17A/QP-5050) in an apparatus equipped with a fused silica capillary column (100% dimethyl polysiloxane (DB-1), internal diameter 0.32 mm, length 60 m, film thickness 1.0 µm). These measurement systems were automated. Analytical results were obtained continuously, at every hour, without the need for manual intervention. In addition, the separating analysis of m-xylene and p-xylene was not made in their GC condition.

III. Results and discussion

BTEX has been generally assumed to originate primarily from the same anthropogenic sources, with the greatest fraction derived from vehicle emissions [39-48]. In this study, the analysis of BTEX concentrations at the two sites focused on whether their characteristics behave as a reflection of the nature of the collecting sites—roadside or residential area. Moreover, stabilities of VOCs in Tokyo are also considered in the context of their numerical lifetimes. The estimated lifetimes [10, 27, 50] of benzene, toluene, ethylbenzene, m-xylene, p-xylene, and o-xylene are 9.4 days, 1.9 days, 1.6 days, 11.8 h, 19.4 h, and 20.3 h, respectively, assuming [OH] = 10^6 molecules/m^3.

Fig. 1 Location of sample collection sites in Tokyo. Road side site (Hachimanyama) and residential site (Shirogane).
First of all, we need to understand the ambient conditions in Tokyo. Fig. 2 shows the monthly variations of oxides of nitrogen (NOx) concentrations at Hachimanyama (roadside) and Shirogane (residential area) in Tokyo, Japan in 2001, which would be typically influenced by the metrological factors including temperature, wind speed, solar radiation and so on relating to atmospheric stability because NOx may relatively be stable compared with other pollutants. The concentrations at at Hachimanyama (roadside) were observed to be very higher than the ones at Shirogane (residential area). The seasonal changes in the concentration were characterized to be high in winter and low in summer in general.

1. Monthly variation in benzene concentrations

Benzene is a ubiquitous compound in urban air, and there is a strong desire to reduce its emission because it is carcinogenic. We examined the monthly variations in benzene at the two monitoring sites, the roadside (Hachimanyama) and residential area (Shirogane), in 2001 (Fig. 3). The data shown here were averaged for each month of year, over a total of about 720 sampling hours. The other VOCs, which will be shown and discussed in this paper later, are treated similarly.

Benzene concentrations, as shown in Fig. 3, ranged from 3.2 to 4.4 µg/m³ (average: 3.6 µg/m³) at the roadside site, and from 2.1 to 2.9 µg/m³ (average: 2.5 µg/m³) in the residential area. The air quality standard for benzene is 3 µg/m³. The levels in the residential area satisfied this criteria; however, the concentrations were higher at the roadside. The roadside site is located very closely to a heavily trafficked road; the readings were therefore strongly influenced by vehicle emissions.

The monthly variations show two peaks—in June and November. The high concentration in June suggested that the unburned and evaporated components of vehicle emissions may contribute to the rise, which implies that the higher summer temperatures accelerated benzene emission as well as metrological conditions. But the exact reason for this needs more investigation. Moreover, atmospheric conditions in Tokyo are known to be very stable in November as NOx concentration rising shown in Fig. 2. These conditions will result in the peaks at two sites in November in monthly variations.

The data in this study were at lower in comparison with other urban cities, i.e., 2.0–6.0 µg/m³ in Texas [45], 2.0–4.0 µg/m³ in Hong Kong [19], 3.2 µg/m³ in Seoul [43], 4.6 µg/m³ in Sao Paulo [51], 6.9 µg/m³ in Berlin [50], and 9.6 µg/m³ in Algeria [52].
2. Monthly variation in toluene concentrations and the ratio of toluene to benzene

Toluene concentrations, as shown in Fig. 4, ranged from 17.1 to 35.8 µg/m³ (average: 22.4 µg/m³) at the roadside and from 11.9 to 32.2 µg/m³ (average: 20.2 µg/m³) in the residential area. Almost all cities display a typical BTEX pattern, in which toluene is the highest, followed by benzene, m,p-xylene, o-xylene, and ethylbenzene [4, 8, 10]. In this study, the order is similar, except that ethylbenzene was higher than benzene.

In contrast to the other VOCs, toluene levels increased greatly in autumn and winter. Moreover, the levels were the lowest at both sites during summer. The seasonal distributions of urban VOCs are controlled by a combination of emission factors, dispersion conditions, and chemical mechanisms. This balance will be more or less favorable to lost processes or emission processes, depending on local characteristics such as site typology and meteorological conditions.

The high autumn–winter levels observed were attributed to weaker vertical and horizontal mixing, and slower chemical destruction rate [10, 27, 50]. Atmospheric conditions in Tokyo are known to be very stable in late autumn and early winter. Air pollutants, including NOx and suspended particulate matter, are commonly known to show this type of seasonal pattern [50].

The concentration levels of toluene were similar between the two sites. The toluene concentration at the residential site was comparable to that of the roadside site, although the other VOCs examined in this study are lower at the residential site. This means that toluene has been emitted by sources other than vehicle exhaust, such as evaporation from fuel, painting, printing, solvent usage, and industrial processes. These considerations have some influence on the characteristics. Moreover, there is more photochemical consumption of toluene in summer due to a higher abundance of the hydroxyl radical (OH). This is considered to be another reason for the trend in addition to the discussion on sources.

The comparison of previously reported toluene concentration data in other urban cities is 4–36 µg/m³ in Hong Kong [19], 27 µg/m³ in Taiwan [14], 28 µg/m³ in Sao Paulo [53], 30 µg/m³ in Santiago [53], 31 µg/m³ in Hamburg [54], 34 µg/m³ in Sydney [54], 41 µg/m³ in Vienna [56], 54 µg/m³ in Athens [57], and 39.2 µg/m³ in Algeria [52]. The levels in this study seemed to be lower than those.

Fig. 5 shows the ratio of toluene to benzene (T/B) at the two sites on a monthly basis. The T/B ranged from 5.0 to 8.1 (average: 6.2) at the roadside and from 4.5 to 13.3 (average: 10.7).
Previously, high values of T/B were observed in Asian cities [10, 14, 19, 41, 50], such as Manila (T/B = 10), Bangkok (T/B = 10), Korea (T/B = 6). However, values of around 2–3 were reported in many cities, such as Algeria, Cairo, and southern Taiwan. In Hong Kong, the range of T/B was around 5 and, in another report, 3–8 in winter and 5–14 in summer.

Lee et al. [19] suggested that T/B increases with increasing traffic volume, industrial emissions, and other urban sources in denser areas. The higher values observed in Asian countries can be understood from this. However, the situation in this study is different from that in Asian countries. The regulation of benzene content in gasoline has been strictly enforced in Japan. Therefore, benzene concentrations were greatly reduced, resulting in a much higher T/B in Tokyo.

3. Monthly variation in xylene concentrations and the ratio of m,p-xylene to o-xylene

Fig. 6 shows the monthly variations of m,p-xylene concentrations at the two sites. They ranged from 5.0 to 10.0 µg/m³ (average: 6.3 µg/m³) at the roadside and from 3.6 to 6.4 µg/m³ (average: 4.6 µg/m³) in the residential area. The monthly variations for both sites show two peaks—in June and November. The reason is similar to the discussion with respect to benzene.

In the comparison with previously reported data, the data in this study seemed to be lower: 3.0–15 µg/m³ in Hong Kong [19], 6.5 µg/m³ Taiwan [14], 6.5 µg/m³ in Chicago [58], and 7.5 µg/m³ in Berlin [50].

Fig. 7 shows monthly variations of o-xylene, another xylene isomer, concentrations at the two sites. They ranged from 1.9 to 3.6 µg/m³ (average: 2.3 µg/m³) at the roadside and from 1.4 to 2.2 µg/m³ (average: 1.7 µg/m³) in the residential area. They also showed the peaks in June and November in the monthly variations for both sites. The levels of o-xylene were similar in other urban cities: 1.5–3.0 µg/m³ in Hong Kong [19], 2.2 µg/m³ in Bombay [59], 2.9 µg/m³ in Berlin [50], and 3.5 µg/m³ in Seoul [43].

Fig. 8 shows the monthly variations of the ratio of m,p-xylene to o-xylene at the two sites. The relation between o-xylene and m,p-xylene was paid special attention by Monod et al. [50]. They reported that m-xylene/p-xylene and m-xylene/o-xylene correlated very well for all samples in urban air, traffic air, and liquid fuel in places that included Paris, Santiago, Hong Kong, 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; however, it can be easily calculated as 3.12.

In this study, the ratios between m,p-xylene to o-xylene were observed to be a constant value of about 2.7 at both sites throughout the year with the exception of June, July, and August—only at the residential site. There are two features in our findings; one is that the ratio is as small as about 87% of the value obtained by Monod et al. [50], although the constancy was kept. The reason of the difference is not understood in this limited research field. The constant ratio will be derived from the fact that o-xylene and m,p-xylene are isomers. Their boiling points are close—being between 138.4–144.5°C [50]. Therefore, they will evaporate simultaneously in the environment. Moreover, it is possible for these compounds to behave similarly in the combustion processes because, as isomers, their chemical properties may be similar.

Another feature is that the ratio decreased in summer. It is a new finding, and is interpreted as follows: the ratio is defined as (m-xylene and p-xylene)/o-xylene. The ratio of lifetimes of m-xylene, p-xylene and o-xylene are 0.58:0.96:1.00 [10, 27, 50], which implies that the lifetime of m-xylene is shorter by a factor of about 60% than that of p-xylene and o-xylene. In summer, m-xylene will disappear...
due to the reaction with OH radical produced under strong sunlight, causing a decrease in its amount. Fig. 9 shows the scatter relation between m,p-xylene and o-xylene at the two sites in July and December. The depression of m-xylene caused by photochemical reactions in July is more clearly shown there. Several intensive papers [61-64] have been published with respect to behavior of hydrocarbons in Osaka, Japan, which showed the complicated regional characteristics on the ambient photochemical reactions.

4. Monthly variation in ethylbenzene concentrations and the ratio of selected VOCs to ethylbenzene

Fig. 10 shows the monthly variations of ethylbenzene concentrations at two sites. They ranged from 2.9 to 6.8 µg/m$^3$ (average: 3.8 µg/m$^3$) at the roadside and from 2.5 to 4.9 µg/m$^3$ (average: 3.4 µg/m$^3$) in the residential area. In this case, no significant difference in ethylbenzene concentrations was observed between the two sites, although that of the roadside site is slightly higher than at the residential site. This is similar to the variation pattern in toluene.

These levels seem to be lower in comparison with those in other urban cities: 2.0–4.0 µg/m$^3$ in Hong Kong [19], 2.6 µg/m$^3$ in Chicago [58], 2.8 µg/m$^3$ in Berlin [50], 6.0 µg/m$^3$ in Sao Paulo [54], 6.5 µg/m$^3$ in Santiago [54], and 6.3 µg/m$^3$ in Algeria [52].

Table 1 shows the ratios of selected VOCs to ethylbenzene. The lifetime of ethylbenzene was estimated to be relatively longer among the BTEX components. The ratios of individual BTEX components to ethylbenzene are often used as an important index in evaluating emission sources and the proximity of fresh emissions [50, 55]. Nelson and Quigley [55] reported that the ratio of m,p-xylene to ethylbenzene was a constant across different sources such as vehicle exhaust, solvent petrol, and fuel evaporation. They found a m,p-xylene to ethylbenzene ratio of about 3, at the 50 percentile value in the frequency distribution observed in Sydney, for air taken at 0600 h. This study obtained 1.67 at the roadside site and 1.35 at the residential site, which are lower than the value in Sydney. This suggests that the ethylbenzene concentration is relatively high in Tokyo, and sources other than vehicle emissions such as those from the use of solvents might contribute to the level of ethylbenzene in Tokyo.

The ratios of toluene to ethylbenzene are close at both sites. This suggests that toluene and ethylbenzene would be emitted by common sources in Tokyo. The other ratios are smaller at the residential site than at the roadside site. Traffic and industrial emissions are transported to the residential site, and pollutants are reduced during dispersion. Therefore, the ratios are low at the residential site.

Table 1 The ratio of selected volatile organic compounds to ethylbenzene at Hachimanyama (roadside) and Shirogane (residential area) in Tokyo, Japan in 2001

<table>
<thead>
<tr>
<th>Site character</th>
<th>m,p-xylene Ethylbenzene</th>
<th>o-xylene Ethylbenzene</th>
<th>Toluene Ethylbenzene</th>
<th>Benzene Ethylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>SD</td>
<td>Average</td>
<td>SD</td>
</tr>
<tr>
<td>Hachimanyama</td>
<td>1.67</td>
<td>0.12</td>
<td>0.62</td>
<td>0.05</td>
</tr>
<tr>
<td>Shirogane</td>
<td>1.35</td>
<td>0.09</td>
<td>0.50</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Ⅳ. Conclusion

Atmospheric benzene, toluene, ethylbenzene, and xylene were characterized on the monthly average basis. Extensive VOCs data, which were measured in Tokyo by the Bureau of the Environment, Tokyo Metropolitan Government in 2001, were examined. As a result, followings were compiled:

1. The monthly variations of these compounds showed two peaks in June and November. The high concentrations in June were considered to be derived from the unburned and evaporated components of fuel which may be accelerated with raised ambient temperature. The high levels observed in November were attributed to weaker vertical and horizontal mixing, and slower chemical destruction rate.

2. Toluene levels increased greatly in autumn and winter. Moreover, the levels were the lowest at both sites during summer. The monthly pattern was greatly different from other VOCs.

3. The concentrations of benzene and xylene were higher
at the roadside than that at residential site through the monthly variations in a year. These readings were considered to be strongly influenced by vehicle emissions.

4. The difference between concentrations at the both sites was small with respect to toluene and ethylbenzene in contrast. Their sources may be not only vehicles but also some stationary sources, such as evaporation from fuel, painting, printing, solvent usage, and industrial processes.

5. The ratios between m,p-xylene to o-xylene were observed to be constant throughout the year with the exception of June, July, and August only at the residential site. In summer, m-xylene will disappear due to the reaction with OH radical produced under strong sunlight, causing a decrease in its amount.

V. Acknowledgments

The authors would like to appreciate their providing the detailed information of air quality monitoring data by members of Bureau of Environment, Tokyo Metropolitan Government.

References


6) Morrow NL. Significance of 1,3-butadiene to the US air toxics regulatory effort. Chemico-Biological Interactions 2001; 135-136, 137-143.


18) Khoder MI. Ambient levels of volatile organic compounds in the atmosphere of Greater Cairo. Atmospheric Environment 2007; 41: 554-566.
30) Fielder RJ. Risk assessment of butadiene in ambient air, the approach used in the UK. Toxicology 1996; 113: 221-225.
33) USEPA, 2002a. Health Assessment of 1,3-butadiene. U.S. Environmental Agency Report EPA/600/P-98/001F.
40) Gin Y, Tonnesen Z, Wang Z. Weekend/weekday differences of ozone, NOx, CO, VOCs, PM10 and the


56) Lanzesterfor Ch, Puxbaum H. Volatile hydrocarbon in and around Vienna, Austria. Water Air Soil Pollution 1990; 41: 345-355.


