Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong

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Abstract

The assessment of volatile organic compounds (VOCs) has become a major issue of air quality network monitoring in Hong Kong. This study is aimed to identify, quantify and characterize volatile organic compounds (VOCs) in different urban areas in Hong Kong. The spatial distribution, temporal variation as well as correlations of VOCs at five roadside sampling sites were discussed. Twelve VOCs were routinely detected in urban areas (Mong Kok, Kwai Chung, Yuen Long and Causeway Bay). The concentrations of VOCs ranged from undetectable to 1396 \( \text{g/m}^3 \). Among all of the VOC species, toluene has the highest concentration. Benzene, toluene, ethylbenzene and xylenes (BTEX) were the major constituents (more than 60% in composition of total VOC detected), mainly contributed from mobile sources. Similar to other Asian cities, the VOC levels measured in urban areas in Hong Kong were affected both by automobile exhaust and industrial emissions. High toluene to benzene ratios (average T/B ratio = 5) was also found in Hong Kong as in other Asian cities. In general, VOC concentrations in the winter were higher than those measured in the summer (winter to summer ratio > 1). As toluene and benzene were the major pollutants from vehicle exhausts, there is a necessity to tighten automobile emission standards in Hong Kong. © 2002 Published by Elsevier Science Ltd.

Keywords: VOCs; Urban area; BTEX ratio; BTEX correlation

1. Introduction

As the air quality becomes increasingly deteriorated in cities world-wide and people were concerned for their health, air quality monitoring has extended beyond the criteria pollutants (carbon monoxide, sulphur dioxide, oxide of nitrogen, ozone and particulate matter) to include measurements of some toxic air pollutants (TAPs) such as volatile organic compounds (VOCs). Emissions of a large number of anthropogenic volatile organic compounds (VOCs) are prevalent in urbanized areas. VOCs play an important role in the formation of ozone and photochemical oxidants associated with urban smog. Interest in determining the VOCs in the atmosphere has increased over the last several decades. Researches have focused on the urban levels of VOCs, especially aromatic and chlorinated organic compounds, due to the known and suspected carcinogenic nature of these species.

Hong Kong is one of the most crowded cities in the world, with more than 6.8 million people, and up to 558 000 gasoline or diesel-run motor vehicles registered in 1997 (Traffic and Transport Survey Division,
Large amounts of VOCs are released from both stationary and mobile sources everyday. Control measures had been taken by the Hong Kong Environmental Protection Department (HKEPD) to control toxic air pollution. In 1993, the HKEPD measured nine VOCs at three locations at typical mixed residential and industrial areas of Hong Kong in order to obtain preliminary data on VOCs. In 1994, the proposed interim guidelines for specific VOCs were published to provide VOC limits based on the effects on relevant health data. In 1997, two toxic air pollutants monitoring stations were set up. An indoor and outdoor air quality comparison study (Lee and Chan, 1988; Lee, 1997) showed that benzene and toluene concentrations in Hong Kong are comparative higher than the other countries. High levels of benzene and toluene in urban areas might be emitted by automobile. The other pollutants such as xylene, ethylbenzene, styrene, tetrachloroethene were found in similar proportions to one another at different sites in Hong Kong. A preliminary study of VOC in Guangzhou, Hong Kong and Macau revealed that organic compounds produced from incomplete combustion of fossil fuels, especially from vehicular exhaust, predominated both in aerosol and VOCs in these samples. However, geological dust and modern living plants also contributed to the toxic organic pollutants (PAHs, BTEX and chlorinated hydrocarbons) in ambient air. In addition, the contribution of emission from kitchen is likely significant due to the characteristic Chinese stir-frying cooking process (stove and food). However, few VOC measurements and variation trend studies related to Hong Kong were performed and the other VOCs listed in USEPA Method TO-14 were not concerned in the past studies.

The objective of this research is aimed to investigate the variation of VOCs concentrations at five urban sites and to characterize the source profiles of VOCs in Hong Kong.

2. Experimental

2.1. Sampling sites and descriptions

In order to investigate the spatial distribution of VOCs in different land use areas, five sites were selected based on their different land use categories, populations and traffic densities. As shown in Fig. 1, five sampling sites including Mong Kok, Causeway Bay, Kwai Chung, Yuen Long and Hok Tsui were selected for VOC monitoring. Their traffic volume and location of the sampling sites were presented in Table 1 and the field descriptions were given as follows:

Mong Kok (MK): It is an urban residential area with high density of population and traffic. Buildings are old and have many ground level shops.
2.2. Sampling

Sampling was conducted at five other sites (MK, CB, KC, YL and HT) in morning rush hours (8:00–9:00 a.m.) from September 1997 to September 1999 for understanding the spatial distribution and seasonal variations of VOCs in Hong Kong. Ten samples were collected on winter (December and January) and summer (July and August) months separately and total 20 samples were collected from each site. The sampler consisted of a pre-evacuated SUMMA canister with a vacuum gauge and a critical orifice controller. The sampling flow rate was adjusted to sample approximately 2.7 l/min for 15 min and was calibrated against a SKC Air Flow Calibrator. Sampling canisters were cleaned by repeated evacuating and filling of humidified zero air for 4–5 circles. All ambient samples were collected from a height of 1.2 m with the pre-cleaned stainless steel canisters. All sample analyses were completed within one week after collection.

2.3. Analytical methodology

Sampling and measurements of 12 VOCs in ambient samples were conducted in accordance with the USEPA Method TO-14 (USEPA, 1997). Air samples were analyzed using a combined cryogenic concentrator (NU-TECH 3350A, USA) with gas chromatograph (HP 6890A) fitted with MSD (HP 5973). Two hundred and fifty ml of sample was loaded and the target compounds were trapped in the cryogenic concentrator with liquid nitrogen. The analytes were desorbed rapidly from −190 to 150 °C. For GC–MS, a capillary column (Restek RTX-1 column, 60 m × 0.32 mm ID × 0.3 μm) was used with an initial oven temperature of −30 to 80 °C at a rate of 10 °C min⁻¹ and then was raised to 220 °C at a rate of 5 °C min⁻¹ (held for 5 min). A calibration curve was built for each of the compounds calibrated at five different concentrations. Correlation coefficients ranged from 0.9823 (methylene chloride) to 0.9999 (toluene). Response linearity tests showed that response signal was proportional to injection volume (50–250 ml) or VOC concentrations (0.1–12 ppbv). Method detection limits (MDLs) for each of compounds were assessed using 10 ppbv of mixed standards in six sampling canisters. MDLs ranged from 0.06 to 0.40 ppbv for 38 mixed standards, and from 0.06 to 0.20 ppbv for the target compounds in this study. For each batch of samples, reproducibility check was performed using duplicated sample analysis. The relative average deviation of two runs in all cases was within ±10%. Zero air (blank) tests were carried out both in the field and laboratory to check contaminant levels.

3. Results and discussion

One hundred samples were collected during the period from September 1997 to September 1999 at five sampling sites. Thirty out of the 42 compounds listed in the Compendium Method TO-14 were below the limit of detection. Most of these VOCs are the most reactive compounds and may be offset in part by removal from the atmosphere due to reactions with the hydroxyl radical and with ozone. Table 2 lists a summary of the 12 VOCs which have been detected and quantified. Significant variations exist in the data at each sampling location and distributions of these VOC compounds are very different at the four urban sites. Toluene, m,p-xylene, and benzene are common top three species in all the four sites and contribute around 50–70% of total VOCs at these urban sites. It showed that traffic emissions are the most important sources in Hong Kong.

3.1. Comparison of VOC emission for each urban locations

Five sampling locations (Mong Kok, Kwai Chung, Causeway Bay and Yuen Long and Hok Tsui) were chosen to represent urban residential area, industrial area, commercial area, newly developed area and background station, respectively.
Table 2
Average concentrations of 12 VOC species at urban and background locations

<table>
<thead>
<tr>
<th>Compounds</th>
<th>MK (n = 20)</th>
<th>KC (n = 20)</th>
<th>YL (n = 20)</th>
<th>CB (n = 20)</th>
<th>HT (n = 20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene chloride</td>
<td>1.40 ± 1.32</td>
<td>39.68 ± 80.34</td>
<td>1.29 ± 1.41</td>
<td>3.79 ± 7.65</td>
<td>1.65 ± 2.14</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.13 ± 1.04</td>
<td>0.68 ± 0.54</td>
<td>0.66 ± 0.75</td>
<td>1.04 ± 1.21</td>
<td>0.87 ± 2.51</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>0.85 ± 0.96</td>
<td>84.49 ± 194.72</td>
<td>1.34 ± 2.55</td>
<td>1.26 ± 2.43</td>
<td>0.27 ± 0.51</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>67.08 ± 137.26</td>
<td>25.38 ± 101.28</td>
<td>1.92 ± 2.22</td>
<td>3.85 ± 3.46</td>
<td>1.87 ± 3.33</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>2.41 ± 2.32</td>
<td>1.28 ± 1.16</td>
<td>0.75 ± 0.72</td>
<td>0.52 ± 0.51</td>
<td>0.22 ± 0.19</td>
</tr>
<tr>
<td>Benzene</td>
<td>15.11 ± 22.95</td>
<td>15.07 ± 16.60</td>
<td>10.53 ± 10.81</td>
<td>10.05 ± 7.24</td>
<td>2.75 ± 1.51</td>
</tr>
<tr>
<td>Toluene</td>
<td>137.15 ± 195.14</td>
<td>139.35 ± 263.98</td>
<td>45.20 ± 50.97</td>
<td>71.10 ± 65.13</td>
<td>4.58 ± 3.26</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>11.65 ± 18.48</td>
<td>24.68 ± 68.56</td>
<td>7.44 ± 8.51</td>
<td>13.70 ± 20.71</td>
<td>2.20 ± 4.11</td>
</tr>
<tr>
<td>m,p-Xylene</td>
<td>22.45 ± 36.99</td>
<td>27.88 ± 54.32</td>
<td>12.27 ± 19.06</td>
<td>13.47 ± 13.23</td>
<td>2.68 ± 2.40</td>
</tr>
<tr>
<td>1,1,1-Dichloroethane</td>
<td>1.43 ± 0.75</td>
<td>7.05 ± 9.03</td>
<td>1.36 ± 1.20</td>
<td>5.11 ± 14.47</td>
<td>nd</td>
</tr>
<tr>
<td>Styrene</td>
<td>3.35 ± 5.30</td>
<td>7.20 ± 15.68</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

Mong Kok (MK) is the most populated and heavy trafficked area in Hong Kong. BTEX (Benzene, toluene, ethylbenzene, m,p-xylene and o-xylene) are mainly from traffic emissions. However, tetrachloroethene was sometimes found to be as high as 409.5 µg/m³ and the average concentration was 67.1 µg/m³. It is possible that tetrachloroethene was emitted from uses of cleaners, especially from the dry-cleaning shops along with the streets.

Compared to MK station, majority of VOCs at CB and YL were lower due to the relatively low traffic volume at the two sites. On the other hand, VOC levels at CB are slightly higher than those at YL station probably due to the poor dispersion at CB.

The VOC spectrum at KC site was distinctively different from the other stations. Most industries in Hong Kong are centralized in this region, especially metal and printing industries. As shown in Table 2, KC has the highest VOC emissions (total median 386.13 µg/m³) among all the studied areas. The average concentrations of chlorinated compounds, such as methylene chloride, tri- and tetrachloroethene, were 39.68, 84.49 and 25.38 µg/m³, respectively and their maximum values were up to 355.27, 895.56 and 455.53 µg/m³, respectively. Since KC is far from the residential area, these chlorinated compounds were released mainly from the factories in this region, for example, degreasing of parts, solvent evaporating during cleaning process, and so on. Even though KC was a relatively open site and has lower traffic volume, its BTEX emissions have higher concentration levels than those in MK. It implied that much BTEX in KC were emitted from industrial sources mixing with the emissions from motor vehicles.

3.2. Comparison of VOC levels with other cities

The daily average concentrations of benzene, toluene, ethylbenzene, m,p- and o-xylanes (BTEX) were compared with other cities commonly discussed in most of studies (Edgerton et al., 1989; Gee and Sollars, 1998). As shown in Fig. 2, Manila and Bangkok have the highest concentrations of toluene, ethylbenzene and xylenes. It is relevant to indicate that many industries are mixed with residential areas. However, the average benzene concentration (13 µg/m³) in Hong Kong were similar to those in Manila (13 µg/m³) and Bangkok (19 µg/m³). Compared with Rome, Hong Kong has comparable toluene and ethylbenzene levels. However, the benzene and xylenes in Hong Kong were 50% lower than those measured in Rome. The differences of BTEX ratios among these cities showed that their industrial types and traffic compositions are different from each other. BTEX emission profile described in Fig. 2 showed that Hong Kong is at median ranges among the seven cities.

3.3. Seasonal variations of TVOC concentrations in Hong Kong

In Hong Kong, winter season includes November, December, January and February; while summer season
is from May to August. Temperature in the winter season is usually between 10 and 20 °C, while temperature ranged usually from 25 to 33 °C in the summer season. In Hong Kong, strong monsoon wind and dry weather characterize winter seasons. In the summer, it is hot and humid with occasional showers and thunderstorms. There are tropical cyclones, strong summer monsoon winds, and thunderstorms in summer. Seasonal variations greatly influences the pollutant concentration in atmosphere.

The total concentration of VOCs was obtained by summing the concentrations of individual species detected in this study. The seasonal averages of VOCs were based on 10 samples collected during winter and summer months at each site from September 1997 to September 1999. The seasonal median concentrations of total VOCs (TVOC) for the five sites are shown in Fig. 3. The average concentration of TVOC exhibits a well-defined seasonal pattern, except at KC station. The total concentrations were higher in winter than in summer. But no similar pattern was found at KC station, suggesting that there was another pollutant source during summertime. Table 3 gives the winter–summer concentration ratios of VOC species. It was found that most of ratios at KC site were less than 1 due to much higher industrial emission or pollutant sources in summer. In contrast, the ratios of winter to summer at other stations were usually more than 1, especially at MK station. This could be explained on the basis of meteorological factors.

In general, there were several factors that could affect the concentrations of VOCs in the winter and in the summer. More rainy days in the summertime caused washout effect of pollutants, thus accumulation of VOCs was less than those in the dry winter. VOCs can also be removed by the particulate matter by dry and wet deposition. Chemical removal, especially by OH radicals, is important during the summer. VOC removal is faster in summer than winter as more sunlight and higher temperatures produce higher chemical removal reaction rate. Thus, the winter VOC concentrations were higher than those in the summertime and similar results were found in many other cities (Wathne, 1983; Hartwell et al., 1987; Baek et al., 1997). However, the distances between the monitoring stations—from station to station—from sampling site to site, are not too far from each other. So the abundance of OH radicals is likely not greatly different at the five stations.

Because the effectiveness on ozone formation and health risks for various VOCs species are dissimilar, it is very important to investigate their concentration levels or percentages of total VOC concentration on different sampling sites. The percentages of VOC chemical speciation classes, i.e., aromatic hydrocarbons, chlorinated hydrocarbons and other portion of VOCs species were also summarized in Fig. 4. At the urban sites (MK, CB

| Winter to summer average VOC concentration ratios |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | MK              | KC              | YL              | CW              | HT              |
| Tetrachloroethene | 6.29            | 0.98            | 0.24            | 0.56            | n.v.            |
| 1,3-Butadiene    | 2.25            | 0.39            | 1.62            | 0.66            | 0.55            |
| Benzene          | 6.64            | 3.03            | 2.62            | 2.17            | 1.56            |
| Toluene          | 5.26            | 2.25            | 2.43            | 1.38            | 1.20            |
| Ethylbenzene     | 6.44            | 0.41            | 2.18            | 0.53            | 3.20            |
| m,p-Xylenes      | 8.74            | 0.34            | 2.45            | 1.33            | 2.22            |
| o-Xylene         | 6.88            | 2.89            | 2.41            | 1.01            | 1.61            |
| Styrene          | 11.38           | 0.13            | 0.35            | 1.08            | 0.53            |

Fig. 3. Seasonal variation of TVOC at Hong Kong.

Fig. 4. Percentages of different classes of VOC species at five sampling sites.
and YL), the sum of aromatic contributed to most of VOCs, varied from 67% to 78%, throughout the study period. At the industrial site (KC), aromatic and chlorinated species contributed to 44% and 54% of TVOCs.

3.4. BTEX ratios

BTEX ratios were calculated to compare the VOC emissions among the five sampling sites. The BTEX ratios of Mong Kok, Kwai Chung, Yuen Long, Causeway Bay and Hok Tsui were (1.3:11.5:1.0:2.8), (1.0:10.6:2.1:3.1), (1.4:6.1:1.0:2.6), (1.0:6.9:1.3:2.1) and (3.3:6.3:1.3:1.0), respectively. The ratio of BTEX reported in the other studies for vehicle exhaust was (3.4:1.4), while in recent studies in the Lincoln Tunnel (USA) the ratio was (3.5:1:3). The ratios of BTEX in Hong Kong were different to these ratios that reflected the ratios of on-road vehicle emissions. However, they were very close to the ratios at three urban sites in New Jersey. The ratios of BTEX were (3:14:1:4), (4:11:1:3) and (7:11:1:3) at Newark, Elizabeth and Camden, respectively (Harkov et al., 1983). The results indicate that both exhaust and evaporative emissions are sources contributing to levels of these pollutants in New Jersey. The differences of BTEX ratios showed that Hong Kong has unique emission pattern. The climate, topography, characteristics of vehicle fuel used, orientation and alignment of buildings, industries and roads, etc. may influence the VOC profiles in Hong Kong. It is a complex scenario that requires more data and intensive measurements in order to draw a conclusion. However, the screening ratios showed that the emission characteristics of each district have great differences.

3.5. Toluene to benzene ratios

Toluene to benzene ratio (T/B) is usually reported by researches besides BTEX ratios. T/B ratio ranged from 2 to 10 in Hong Kong. T/B ratios in Kwai Chung, Mong Kok, Causeway Bay, Yuen Long and Hok Tsui were 10.0, 9.1, 7.1, 4.4 and 1.9, respectively. Comparing other cities with the main sources of benzene and toluene were from vehicle exhaust, it is reasonable to explain that there are other sources of toluene in Hong Kong. It is interesting to note that T/B ratio increased as the traffic volume, industrial emissions and other urban sources increased in denser areas. Hong Kong has T/B ratio of about 5.0 while the other cities have T/B ratio of 2.0–3.3. Brocco et al. (1997) found that the T/B ratio in the urban area of Rome ranged from 2.0 to 3.3. Similar ratios of 10 were observed in Asian cities such as Manila and Bangkok (Gee and Sollars, 1998). Kwai Chung and Mong Kok showed similar results with other Asian cities because they all are located in similar area settings with large industrial emissions. It is also believed that there are additional sources of toluene in Kwai Chung and Mong Kok. Overall, Hong Kong and other Asian cities had relatively large T/B ratio. Gee and Sollars (1998) suggested that there are large additional sources of toluene in these cities or that there are major differences in the fuels or vehicles used. It is clear that unleaded fuels that are widely used in Asian cities including Hong Kong contain very high aromatic level (45%).

3.6. BTEX correlations

As shown in Table 4, BTEX correlations were evaluated at the five districts. Good BTEX correlation ($R^2 > 0.8$) was found in Hok Tsui. This background site, with no nearby point sources to skew the correlation, received pollution from the region that was predominantly related to the automobile. Mong Kok and Yuen Long had significant correlations among the BTEX.

Good correlations among TEX and poor correlation of benzene with TEX were found in Kwai Chung, TEX mainly came from traffic emission, painting and industrial solvents while benzene mainly came from traffic source. Since there were two complicated sources for BTEX in Kwai Chung, it was reasonable to expect a poor correlation. Causeway Bay had poor BTEX correlation. The poor correlation can be explained by the mixed sources of BTEX that appeared at different times or that some sources of BTEX only emitted at a certain time, such as the evaporation of solvents during cleaning processes.

Benzene was well correlated with other aromatic VOCs at Hok Tsui, Mong Kok and Yuen Long. As discussed above, benzene and other aromatic hydrocarbons were predominantly from motor vehicle exhaust. Thus, benzene can be used as an indicator for other aromatic hydrocarbons in heavy traffic areas. The correlation between benzene and toluene at each station was plotted in Fig. 5. Mong Kok and Yuen Long had slope (toluene to benzene ratio (T/B)) of 4.6. However, it was obvious that Mong Kok had more additional sources of toluene or their background levels of toluene were much higher than that of Yuen Long. As mentioned above, Kwai Chung is an area with much VOC emission from different kinds of industries; thus, it has a higher background level of toluene ($R^2 < 4$). In Mong Kok, traffic jam frequently occurred which caused accumulation of pollutants and toluene has shorter half-life in the atmosphere, therefore higher toluene background levels were measured. Higher T/B ratio (5.5) was found in Causeway Bay than in other urban areas, while T/B ratio of 1.2 was found in Hok Tsui.
4. Conclusion

The concentrations of VOCs at five urban sites in Hong Kong were quantified by using canister with GC/MS system in accordance with the USEPA Method TO-14. The accuracies of VOCs analysis were validated with quality assurance and quality control (QA/QC) procedures. VOCs (1,3-butadiene, methylene chloride, chloroform, trichloroethene, tetrachloroethene, 1,1,1-trichloroethane, benzene, toluene, ethylbenzene, m,p-Xylenes, o-Xylene) were identified at roadside urban areas in Hong Kong. The concentrations of VOCs ranged from undetectable to 1396 μg/m³. Among all of the VOC species, toluene has the highest concentration. High concentrations of chlorinated compounds were found at Kwai Chung where it is located in an industrial area with industrial emissions. Hok Tsui served as a background station with VOC concentrations less than 10 μg/m³ since there were no significant anthropogenic sources. Benzene, toluene, ethylbenzene and xylene (BTEX) were mainly from vehicle exhausts, while chlorinated compounds were mainly from industries, cleaning processes and chemical solvents. However, mixed sources were frequently observed at Mong Kok and Causeway Bay. The concentrations of VOCs in Hong Kong were similar to other cities in the world. However, the ratios of T/B (average T/B ratio = 5) were higher in Hong Kong than that of other cities (average T/B ratio = 2 or 3). The morning concentration ratios were varied at different locations. In general, VOC concentrations mirrored those of other cities in that VOC concentrations were higher in winter than in summer. Hong Kong has a unique VOC emission pattern due to the unique climate, topography and the density of vehicles and population. Thus, the VOC profiles, such as BTEX ratios and temporal variations were different from other urban cities. Given that toluene and benzene were the major cancer causing pollutants from vehicle
exhaust, there is a need to tighten emission standards for such toxic compounds.

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