One-year monitoring of aromatic volatile organic compounds (VOCs) in urban areas of Malaysia

N S S L Hawari¹, M T Latiff¹*, M Othman², N M Hanif³, H H A Hamid¹, N I H Mustaffa¹, A A A Mohtar

¹Department of Earth Sciences and Environment, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia
²Institute for Environment and Development (LESTARI), Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia
*Corresponding E-mail: talib@ukm.edu.my

Abstract. VOCs have been one of the important limiting factors of O₃ photochemical production in the urban tropical region. This study aims to determine the variation and composition of aromatic VOCs as well as their contribution to the O₃ formation. The hourly data of benzene, toluene, ethylbenzene and xylenes (BTEX) and ozone (O₃) were retrieved from January until December 2019 at three continuous air quality monitoring stations (S1, S2 and S3) operated by the Malaysian Department of Environment (DOE). Aromatic VOCs is detected by using an online gas chromatography analyser (GC 5000BTX). The annual average ΣBTEX concentrations ranged from 14.53 ± 12.43 µg m⁻³ to 25.04 ± 24.04 µg m⁻³ during the observation period, with toluene as the most dominant species with an average concentration of 10.65 ± 12.12 µg m⁻³. The O₃ formation potential (OFP) was calculated and the results indicated that toluene is the highest contributor of O₃-forming potential, followed by m,p-xylene, o-xylene, ethylbenzene and benzene with the value of 127.8 μg m⁻³ (40.90 %), 103.0 μg m⁻³ (32.97 %), 48.66 μg m⁻³ (15.58 %), 26.17 μg m⁻³ (8.38 %) and 6.74 μg m⁻³ (2.15 %), respectively. Since the study of VOCs in Malaysia is quite limited, a more comprehensive study is currently underway to integrate the research on variation of VOCs in ambient air and its impact on the environment and human health.

Keywords: BTEX, Volatile Organic Compounds, Ozone Formation Potential, Urban areas

Track Name: Atmospheric Chemistry and Physics

1. Introduction

Volatile organic compounds (VOCs) have been one of the important limiting factors of ozone (O₃) photochemical production in the urban tropical region. Considerable efforts have been expended in recent times to understand the tropospheric O₃ formation mechanism, which is usually produced from photochemical reactions involving VOCs with various atmospheric radicals (i.e., OH radicals, HO₂ radicals, etc.) [1-4]. Anthropogenic VOCs emissions are complex and vary from city, with primary sources including automobile exhaust, gasoline volatilisation, solvent usage, industrial and domestic coal combustion and biomass burning, whereas additional sources are mainly affected by regional
transport [5-7]. Anthropogenic VOCs, generally referred to as aromatic hydrocarbons, are the most frequently measured by previous studies. Aromatic VOC, particularly benzene, toluene, ethylbenzene and xylenes (BTEX) partitions is of great concern as it may cause a detrimental impact on human health [8-11]. The nature and extent of these health risk effects depend on the concentration levels of the species and the duration of their exposure to pose adverse health effects [12]. According to Ran et al. [13], atmospheric VOCs may exacerbate both respiratory and cardiovascular disease, particularly congestive heart failure (CHF) and chronic obstructive pulmonary disease (COPD).

BTEX is commonly considered as the key precursor to major air pollutants. Hot spot areas, typically urban areas, are ideal for studying BTEX emissions where the concentration levels in the atmosphere are significantly higher than the background remote areas [14, 15]. For instance, the urban air of Kuala Lumpur was observed to be slightly more polluted, resulting in health and air pollution issues [16]. Pollution levels in developing countries have dramatically increased in recent years due to a high volume of fresh potential emissions sources with large populations [17, 18].

Herein, this study aims to determine the variation of aromatic VOCs in selected cities in Malaysia and to evaluate its contribution to O3 formation potential (OFP) in ambient air. It is hoped that the findings will help in designing effective mitigation strategies to improve the ambient air quality in Malaysia by providing information about VOCs variation, composition and their contribution. A more comprehensive study is currently underway to integrate the research on variation of VOCs in ambient air and its impact on the environment and human health.

2. Methodology

2.1. Study area

As shown in Figure 1, three monitoring stations were selected in this study: Cheras (S1), Shah Alam (S2) and Seremban (S3) stations. S1 (N 03° 6’ 22.44”, E 101° 43’ 4.5”) and S2 (N 03° 6’ 16.9”, E101°33’22.3”) are located in the Klang Valley basin, whereas S3 (N 02° 43’ 24.1”, E 101° 58’ 6.5”) is situated approximately 67 km from Kuala Lumpur. All cities in this study are categorised as tropical rainforest climate region: hot and humid throughout the year. The elevation height of each station varied between 53 m and 79 m above sea level. The monitoring stations were selected based on the traffic conditions, proximity to the congested highways or streets and geographical distribution. S1 station represents a residential–urban environment and is near major roads and highways. For S2 station, it is a rapidly urbanising area and the most developed state in Malaysia. Meanwhile, the S3 station is the capital state of Negeri Sembilan, situated near the schools and resembles a residential setting.
Figure 1. Map of study area showing S1 (Cheras), S2 (Shah Alam) and S3 (Seremban) as the monitoring stations.

2.2. Continuous sampling
The continuous sampling of aromatic VOCs and O₃ were carried out at three selected monitoring stations starting from January to December 2019. A compact online gas chromatography analyser (GC 5000BTX, AMA Instruments, Germany) is used to measure aromatic VOCs. The GC-5000BTX analyser is capable of capturing ambient aromatic VOCs concentration at a temporal resolution of 30 min. The device was installed with a capillary column AMASep (30 m x 0.32 mm ID, 1.5 µm film thickness) and a flame ionisation detector (FID) to detect VOCs parameters. In this study, five species of aromatic VOCs (benzene, toluene, ethylbenzene, m,p-xylene and o-xylene) were continuously collected on an hourly basis (local time). Prior to analysis, the temperature of the GC was set at 50°C for 3 min, 8°C/min to 130°C and was retained for 5 min. A volume of 30 mL of air will be pumped onto the enrichment tube and pre-concentrated the targeted VOCs before they are thermally desorbed into the GC system to detect BTEX species. Routine quality control (QC) was performed at single point calibration (10 ppb) of VOCs standard gas for the instrument validation performance.

2.3. Statistical data analysis
All statistical analyses were carried out using the Rstudio software - Openair package (version 2.8-3). In this study, the unit of the measurements was converted from part per billion (ppb) to micrograms per cubic metres (µg m⁻³). The missing values (including data outliers) for each sampling station were estimated at 3.99% (S3), 6.54% (S2) and 10.33% (S1). The statistical approach taken in this study omitted missing data values from the calculation to interpret the findings.

2.4. Ozone formation potential calculation
Briefly, calculating the O₃ formation potential (OFP) is one way to represent the relative contribution of VOC species towards the O₃ reactivity. The OFP was computed by multiplying the aromatic concentration with the maximum incremental reactivity (MIR). The MIR scale, comprehensively integrated by Carter [19], is a quantitative reactivity scale that expressed as the mass of additional O₃ formed per mass of VOC added to the emissions of various compounds under various atmospheric conditions. Herein, the updated coefficient value of the MIR scale is used to calculate the OFPs in this
study [20, 21]. Every VOC species quantified a different MIR coefficient value; benzene had a value of 0.72 (g-O₃ g-VOCs⁻¹), toluene had a value of 4.00 (g-O₃ g-VOCs⁻¹), ethylbenzene with 3.04 (g-O₃ g-VOCs⁻¹), m,p-xylene with 7.8 (g-O₃ g-VOCs⁻¹) and o-xylene with 7.64 (g-O₃ g-VOCs⁻¹). The O₃ potential can be calculated based on the following equation:

$$\text{OFP (µg m}^3\text{)} = \text{C}_{\text{VOC}} \times \text{MIR}_i$$

Where;
- $\text{C}_{\text{VOC}}$: Concentration of compound (µg m⁻³)
- MIRᵢ: Maximum incremental reactivity coefficient value (g-O₃ g-VOCs⁻¹)

### 3. Results and Discussion

#### 3.1. Descriptive data

Table 1 presents detailed results obtained from the preliminary analysis of BTEX concentration at the three monitoring stations. The annual average ΣBTEX concentration ranged from 14.53 ± 12.43 µg m⁻³ to 25.04 ± 24.04 µg m⁻³ during the observation period. Toluene was the most dominant species at all stations, with an average concentration of 10.65 ± 12.12 µg m⁻³. In contrast, o-xylene had the lowest concentration at all stations with approximately 2.12 ± 2.02 µg m⁻³. Moreover, the average level of benzene over the year was 3.12 ± 2.85 µg m⁻³. The observed benzene in our study does not exceed the standard benzene value (5 µg m⁻³) as suggested by the Central Pollution Control Board [22, 23]. Taken together, the ambient BTEX concentration was in the following order: o-xylene < ethylbenzene < benzene < m,p-xylene < toluene. A previous study in India demonstrated that the average concentration of BTEX was between 186 ± 107 µg m⁻³ and 456 ± 224 µg m⁻³, with toluene accounting for 42-50 % and benzene accounting for 26-30 % of the total BTEX [24]. Other similar findings by Cruz et al. [25] stated that toluene was the most abundant species amongst the BTEX compounds with the average level ranging from 2.47 ± 1.49 µg m⁻³ to 3.18 ± 0.97 µg m⁻³ in the tropical urban area of Brazil. The high levels of toluene detected in ambient air can be explained by the fact that toluene is frequently added to gasoline to improve vehicle fuel efficiency. BTEX emissions in urban air are commonly caused by gasoline-powered automobile exhaust gas, evaporative emissions generated during the processing, storage, and distribution of gasoline and solvent usage. Intriguing findings by Hosaini et al. [26] identified the possible sources of anthropogenic VOCs in Kuala Lumpur city: motor vehicle exhaust or solvent (21-22%), petrol pump or solvent usage (15%) and industrial emissions (10%).

| Compound       | S1     | S2      | S3      | Average    |
|----------------|--------|---------|---------|------------|
| Benzene        | 3.14 ± 3.07 | 3.28 ± 3.23 | 2.94 ± 2.24 | 3.12 ± 2.85 |
| Toluene        | 12.08 ± 10.50 | 13.59 ± 20.88 | 6.27 ± 4.98 | 10.65 ± 12.12 |
| Ethylbenzene   | 3.38 ± 3.49 | 3.64 ± 3.94 | 1.58 ± 1.56 | 2.87 ± 3.00  |
| m,p-Xylene     | 3.93 ± 4.81 | 6.85 ± 8.18 | 2.43 ± 2.55 | 4.40 ± 5.18  |
| o-Xylene       | 2.50 ± 2.16 | 2.57 ± 2.81 | 1.30 ± 1.09 | 2.12 ± 2.02  |
| ΣBTEX          | 25.04 ± 24.04 | 29.93 ± 39.04 | 14.53 ± 12.43 | 23.17 ± 25.17 |

#### 3.2. Monthly variation of BTEX

The variability of aromatic BTEX concentration for 12 months at the three monitoring stations is illustrated in Figure 2. The maximum average level of BTEX was reported at S2 station with a value of 61.12 µg m⁻³ in July and a minimum of 8.87 µg m⁻³ in February at S1 station. Contrary to
expectations, the BTEX observed showed an unusual trend at the S2 station due to the influence of high levels of toluene and m,p-xylene compared to the other stations over the year. June-July undergoes dry season, which supposedly the BTEX concentration is at a minimum level during this month due to atmospheric dispersion, high intensity and temperatures [27]. This result may be explained by the fact that VOC can vary depending on monsoonal changes / seasonal differences, additional sources, relative reactivities, environmental conditions, etc. Another possible reason that caused the BTEX trend at S2 station was due to the characteristics of the studied areas, sampling points and sampling duration, city activities including emissions from industries, as well as differences in vehicle characteristics (e.g. vehicle manufacturing quality and fuel composition). However, the study is limited by the lack of information on the monthly variation of VOC, particularly BTEX, in other tropical Asian cities.

3.3. Ozone Formation Potential (OFP)
Based on Figure 3, the total OFP for the measured aromatic VOC at the sampling sites varied between 60.92 to 140.7 μg m\(^{-3}\). World Health Organisation (WHO) has prescribed that the air quality guidelines for \(O_3\) levels is below 120 μg m\(^{-3}\) [28, 29]. The leading contributors to \(O_3\) formation during the sampling period are toluene, followed by m,p-xylene, o-xylene, ethylbenzene and benzene with the OFP value of 127.8 μg m\(^{-3}\) (40.90 %), 103.0 μg m\(^{-3}\) (32.97 %), 48.66 μg m\(^{-3}\) (15.58 %), 26.17 μg m\(^{-3}\) (8.38 %) and 6.74 μg m\(^{-3}\) (2.15 %), respectively. Although classified as the most toxic and carcinogenic species among C6-C9 aromatic VOCs [29-31], benzene had the lowest contribution to the \(O_3\) formation mechanism throughout this research work. Overall, toluene and m,p-xylene significantly contributed to the level of \(O_3\) in ambient air at all sampling points. These results were found to be comparable with a study conducted by Hosaini et al. [26] revealed that OFP in ambient Kuala Lumpur is ranked from benzene (6.50 μg m\(^{-3}\)) < ethylbenzene (32.8 μg m\(^{-3}\)) < toluene (135.9 μg m\(^{-3}\)) < o-xylene (139.9 μg m\(^{-3}\)) < m,p-xylene (145.8 μg m\(^{-3}\)). In Delhi, India, the total OFPs concentration was obtained at about 207.5 ± 123.4 μg m\(^{-3}\), with toluene as the main contributor [32]. The major contribution of OFP in Hanoi, Vietnam [12] was the aromatic group (56.8 %): m,p-xylene (15.7 %), toluene (12.0 %), 1,2,4-trimethyl benzene (6.9 %), isopentane (6.3 %) and o-xylene (5.8 %).
The high OFP of VOCs clearly indicates the O₃ pollution issues in the future. For instance, previous research by [31] reported that aromatic VOC (59 %) dominated the high level of OFP and affected the local tropospheric O₃ in China, followed by alkenes and alkynes (26 %), alkanes (9 %) and carbonyl compounds (6 %). To sum up, the results of OFP indicated that aromatic VOCs significant impacts on surface O₃ in urban cities of Malaysia. It is well documented that O₃ in the lower troposphere is directly linked to its precursors, VOC. High ground-level O₃ were often seen in many hotspot cities, such as in Kuala Lumpur city. The O₃ episode events in Malaysia were mainly caused by enhanced precursors emission and meteorological conditions favourable to O₃ production (including higher temperature). This statement is proved with a recent case study by [33] revealed that the total concentration of O₃ episode days in Guanzhong Plain, China was significantly higher than non-episode days, with a value of 33.43 ± 13.64 ppb and 29.13 ± 14.31 ppb, respectively. In view of all that has been mentioned so far, determining the limiting factors of O₃ formation in the target regions is crucial for implementing regional O₃ reduction strategies.

![Figure 3](image_url)

**Figure 3.** Aromatic VOC contributions to the total OFPs at S1, S2 and S3 stations.

4. Conclusion

Aromatic VOCs (BTEX) were continuously observed from January to December 2019. The present study was designed to determine the variation of aromatic VOCs in Malaysia's urban cities and their contribution to the O₃ formation mechanism. A notable finding from this study is that the annual average ΣBTEX concentration was approximately 23.17 ± 25.17 µg m⁻³. All stations showed that toluene was the most dominant species with an average concentration of 10.65 ± 12.12 µg m⁻³. The airborne BTEX concentration was in the following order: o-xylene < ethylbenzene < benzene < m,p-xylene < toluene. Additionally, toluene was also the highest contributors to O₃ formation in ambient air, followed by m,p-xylene, o-xylene, ethylbenzene and benzene. As VOCs play a crucial role in the O₃ forming potential and photochemical oxidants associated with urban smog, it is important to determine the occurrence, sources, and behaviour of VOCs to establish effective air pollution abatement approaches. Therefore, these findings make several contributions to the current literature and provide new insight into the air quality level in Malaysia.
References

[1] Sillman S 1999 The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments Atmos. Environ. 33 1821–1845

[2] Poisson N, Kanakidou M, Bonsang B, Behmann T, Burrows J P, Fischer H, Götz C, Harder H, Lewis A, Moortgat G K, Nunes T, Pio C A, Platt U, Sauer F, Schuster G, Seakins P, Senzig J, Seuwen R, Trapp D, Volz-Thomas A, Zenker T and Zittelberger R 2001 The impact of natural non-methane hydrocarbon oxidation on the free radical and ozone budgets above a eucalyptus forest Chemosphere - Glob. Chang. Biol. 3 353–366

[3] Tong H et al 2019 Radical formation by fine particulate matter associated with highly oxygenated molecules Environ. Sci. Technol. 53 12506–12518

[4] Derwent R G, Jenkin M E, Saunders S M and Pilling M J 1998 Photochemical ozone creation potentials for organic compounds in northwest Europe calculated with a master chemical mechanism Atmos. Environ. 32 2429–2441

[5] Tiwari V, Hanai Y and Masunaga S 2010 Ambient levels of volatile organic compounds in the vicinity of petrochemical industrial area of Yokohama, Japan Air Qual. Atmos. Health 3 65–75

[6] Yadav R, Sahu L, Beig G and Jaafrey S N A 2016 Role of long-range transport and local meteorology in seasonal variation of surface ozone and its precursors at an urban site of India Atmos. Res. 176–177

[7] Ohara T, Akimoto H, Kurokawa J, Horii N, Yamaji K, Yan X, et al 2007 An Asian emission inventory of anthropogenic emission sources for the period 1980–2020 Atmos. Chem. Phys. 7 6843–6902

[8] Atkinson R and Arey J 2003 Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review Atmos. Environ. 37 197–219

[9] Montcro-Montoya R, Lopez-Vargas R and Arellano-Aguilar O 2018 Volatile organic compounds in air: sources, distribution, exposure and associated illnesses in children Ann. Glob. Health 84 225–238

[10] Latif M T, Hamid H H A, Ahamad F, Khan M F, Nadzir M S M, Othman M et al 2019 BTEX compositions and its potential health impacts in Malaysia Chemosphere 2019 237 124451

[11] Pandey P and Yadav R 2018 A Review on Volatile organic compounds (VOCs) as environmental pollutants: fate and distribution Int. J. Plant Environ. 4 14–26

[12] Anchal G and Gupta N C 2018 A comprehensive study on spatio-temporal distribution, health risk assessment and ozone formation potential of BTEX emissions in ambient air of Delhi, India Sci. Total Environ. 659

[13] Ran J, H Qiu, S Sun and L Tian 2018 Short-term effects of ambient benzene and TEX (toluene, ethylbenzene, and xylene combined) on cardiorespiratory mortality in Hong Kong Environ. Int. 117 91–98

[14] Li B T, Kajit Y, Nguyen T Y, Shoji K, Van D A, Do T N, Nghiem T D and Sakamoto Y 2020 Characteristics of roadside volatile organic compounds in an urban area dominated by gasoline vehicles, a case study in Hanoi Chemosphere 254 126749

[15] Pandey P and Yadav R 2018 A review on volatile organic compounds (VOCs) as environmental pollutants: fate and distribution Int. J. Plant Environ. 4 14–26

[16] Chin Y S J, De Pretto L, Thuppil V and Ashfold M J 2019 Public awareness and support for environmental protection-a focus on air pollution in peninsular Malaysia PLoS One 14 e0212206–e0212206

[17] Zhu X, Fan Z T, Wu X, Meng Q, Wang S W, Tang X et al 1994 Spatial variation of volatile organic compounds in a "Hot Spot" for air pollution Atmos. Environ. 42 7329–7338

[18] Dehghani M, Fazlizadeh M, Sorooshian A, Tabatabaea H R, Miri M, Baghni A N et al 2018 Characteristics and health effects of BTEX in a hot spot for urban pollution Ecotoxicol. Environ. Saf. 155 133–143

[19] Carter W P 1994 Development of ozone reactivity scales for volatile organic compounds Air & Waste 44 881–99

[20] Carter W 2010 Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications California Air Resources Board 1 07–339

[21] Venecek M A, Carter W P L and Kleeman M J 2018 Updating the SAPRC Maximum incremental reactivity (MIR) scale for the United States from 1988 to 2010 2018 J. Air Waste Manag. Assoc. 12 1301–1316

[22] Central Pollution Control Board 2009 Ambient Air Quality Standards

[23] Sekar A, Varghese G K and Ravi Varma M K 2019 Analysis of benzene air quality standards, monitoring methods and concentration in indoor and outdoor environment Heliyon 5 02918

[24] Saxena P and Ghosh C 2012 A review of assessment of benzene, toluene, ethylbenzene and xylene (BTEX) concentration in urban atmosphere of Delhi Int. J. Phys. Sci. 7 850–860

[25] Cruz L P S, Santos D F, dos Santos I F, Gomes I V S, Santos A V S and Souza K S P 2020 Exploratory analysis of the atmospheric levels of BTEX, criteria air pollutants and meteorological parameters in a tropical urban area in Northeastern Brazil Microchem. J. 152 104265

[26] Hosaini P N, Khan M F, Mustaffa N I H, Amil N, Mohamad N, Jaafar S A et al 2017 Concentration and source apportionment of volatile organic compounds (VOCs) in the ambient air of Kuala Lumpur, Malaysia Nat. Hazards 85 437–452

[27] Rad H D, Babaei A A, Goudarzi G, Angali K A, Ramezani Z and Mohammadi M M 2014 Levels and sources of BTEX in ambient air of Ahvaz metropolitan city Air Qual. Atmos. Health 7 515–524

[28] World Health Organization 2006 Air Quality Guidelines: Global Update 2005: Particulate Matter, Ozone, Nitrogen Dioxide, and Sulfur Dioxide
[29]Hajizadeh Y, Mokhtari M, Faraji M, Mohammadi A, Nemati S, Ghanbari R, Abdolahnejad A, Fard A R F, Nikoonahad A, Jafari N and Miri M 2018 Trends of BTEX in the central urban area of Iran: A preliminary study of photochemical ozone pollution and health risk assessment Atmos. Pollut. Res. 9 220–229

[30]Duerta-Davidson R, Courage C, Rushton L and Levy L 2001 Benzene in the environment: an assessment of the potential risks to health of the population Occup. Environ. Med. 58 2–13

[31]Ran J, Qiu H, Sun S, Tian L, 2018 Short-term effects of ambient benzene and TEX (toluene, ethylbenzene, and xylene combined) on cardiopulmonary mortality in Hong Kong Environ. Int. 117 91–98

[32]Skov H, Lindskog A, Palmgren F and Christensen C S 2001 An overview of commonly used methods for measuring benzene in ambient air Atmos. Environ. 35 S141–S148

[33]Hui L, Ma T, Gao Z, Gao J, Wang Z, Xue L, Liu H and Liu J 2021 Characteristics and sources of volatile organic compounds during high ozone episodes: a case study at a site in the eastern Guanzhong Plain, China Chemosphere 265 129072

Acknowledgement
This research was supported by the Universiti Kebangsaan Malaysia (UKM) research grant DIP-2019-006 (Dana Impak Perdana) and in collaboration with the Department of Environment Malaysia (DOE).