Anthropogenic and biogenic volatile organic compounds and ozone formation potential in ambient air of Kuala Lumpur, Malaysia

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Abstract. The measurement of anthropogenic and biogenic volatile organic compounds (VOCs) in urban air is important because of their toxic effects and because they can produce secondary air pollutants (e.g. ozone, particulate matter). Benzene, toluene, ethylbenzene and xylenes (BTEX), representing anthropogenic VOCs (AVOCs), and isoprene, a biogenic VOC (BVOC), were monitored at an urban site in Kuala Lumpur (KL). Active sampling was conducted using sorbent tubes packed with Tenax®TA/1 TD for 5 days (daytime). Analysis of VOCs was performed using Thermal Desorption-Gas Chromatography Mass Spectrometry (TD-GCMS). Average daytime concentrations of VOCs were 9.42 ± 6.15 μg/m^3 for benzene, 35.04 ± 12.60 μg/m3 for toluene, 11.20 ± 4.17 μg/m^3 for ethylbenzene, 19.19 ± 10.76 μg/m^3 for m,p-xylene, 18.40 ± 8.56 μg/m^3 for o-xylene, and 6.70 ± 1.57 μg/m^3 for isoprene. Weekday BTEX levels were found to be higher, especially during the morning rush hour, demonstrating the impact of traffic emissions in KL. BVOCs (isoprene) in urban KL was also higher than the reported isoprene level in Malaysian forest areas but lower than palm plantation areas. Both AVOCs and BVOCs significantly contributed to (218.6 – 733.8 μg/m^3) ozone formation in the KL atmosphere.

1. Introduction

Volatile organic compounds (VOCs) can be emitted from anthropogenic and biogenic sources to the atmosphere. Anthropogenic VOCs (AVOCs) such as benzene, toluene, ethylbenzene, and xylene isomers (BTEX) are dominant in the urban atmosphere due to vehicle, industrial, and biomass emissions [1][2][3]. Meanwhile, biogenic VOCs (BVOC), mainly isoprene, are released by plants and vegetation [4][5]. The measurement of AVOCs and BVOCs is important due to their contribution to surface ozone formation, secondary organic aerosol (SOA), the health risk posed to humans, and their

environmental impact [6]. Moreover, BTEX are hazardous air pollutants (HAPs) and benzene is the most toxic and a known carcinogen.

The impacts of isoprene and BTEX on urban air may vary depending on meteorological and regional differences [7][8]. Tropical regions receive high solar radiation throughout the year this may induce photochemical reactions of VOCs and influence VOC levels and atmospheric composition [9]. Isoprene can play a very significant role in ozone formation due to its higher reactivity compared to other BVOCs [10]. Both BVOCs and semivolatile organic compounds (SVOCs) produce SOA which directly and indirectly impacts climate change via solar radiation scattering [11]. Even though BVOCs are known to be emitted at greater levels compared to AVOCs globally, in the case of urban areas, AVOCs may significantly influence the local ambient air [12].

The Kuala Lumpur (KL) urban area, similar to other cities in South East Asia and developing countries, is facing air pollution problems related to heavy traffic [13]. VOCs, including BTEX, are released into the atmosphere and polluted the surrounding areas from incomplete combustion in vehicle engines [14][15]. A Study by Lan & Binh [16] revealed that the benzene level at the roadside in Kuala Lumpur was 48 $\mu g/m^3$. Meanwhile, the outdoor level of benzene in Johor Bahru, another urban city in Malaysia, was measured at 5.1 $\mu g/m^3$ [17]. However, information on BVOCs, i.e. isoprene, in the ambient air of urban KL is still very limited.

This paper aims to evaluate the levels of isoprene and BTEX, representing biogenic and anthropogenic VOCs, in the ambient air of urban KL. Ozone formation potential was also calculated to understand their contribution to surface ozone.

2. Methodology

2.1 Sampling

Sampling was conducted at the Faculty of Health Science, Universiti Kebangsaan Malaysia, Kuala Lumpur (UKM, KL) (N03° 10'5.28", E101° 42'1.56") (Figure 1). The sampling was performed on the 3rd floor (~10 m from the ground) and the building is situated near two major KL roads, Jalan Raja Muda Abdul Aziz and Jalan Pahang. Five days of sampling (30th January 2018 – 3rd February 2018) were undertaken at three daytime intervals; T1 (0800-1000), T2 (1200-1400), T3 (1600-1800). The sampling procedure was based on the active sampling method, using Tenax®TA/1 TD (Markes International, UK) multi-sorbent tubes. A low-flow pump (Personal Air Sampler) PAS-500 (Supelco, US) was set at a flow rate of 60 ml/min and operated for 2 h.

Figure 1. VOC sampling location map in Kuala Lumpur

2.2 *Analysis*

The analysis of the sorbent tubes was performed using thermal desorption (TD) (Markes, International, UK) gas chromatography mass spectrometry (GCMS) (Agilent Technologies, US). The TD-GCMS system was equipped with a DB 624 column (60 m × 0.25 mm × 0.25 µm) (Agilent J&W Scientific, US) for VOC separation. The tubes were thermally desorbed at 280°C for 30min onto the focusing trap at 25°C, and the trap high was performed at 330°C for 3 min to transfer the analytes to the GCMS. The temperature program was set at initial 36°C (4min), with a ramp rate of 5°C/min to 250°C. The measurement of isoprene and BTEX was based on an external calibration. Gas standards of 10 ppm BTEX (MESA, USA) and 100 ppm isoprene (MESA, USA) were diluted with purified nitrogen to several individual BTEX and isoprene concentrations (30-400 ng) in the sorbent tubes for the multiple point calibration. A calibration solution loading rig (CSLR), (Markes, UK) was used as an aid to preparing the standards in the stainless steel sorbent tubes. Calibration linearity results (r^2) for all compounds were good, >0.987. Validation was performed using different standard gases containing 100 ppb of 62 toxic gas VOCs (TO-17 gas standards) (Scotty, US). Recovery for BTEX was found 81-104%.

2.3 *Ozone Formation Potential (OFP)*

OFP can be a reference metric to describe the potential maximum ozone formation in urban areas where VOC-sensitive [18]. The contribution of individual BVOCs and AVOCs to OFP was studied using their Maximum Incremental Reactivity (MIR). According to Duane et al. [19], MIR can be referred to as the maximum amount of ozone produced by the photolysis of specific volatile compounds. OFP can be measured as:

$$\text{OFP } (\mu g/m^3) = \text{concentration } (\mu g/m^3) \times \text{MIR coefficient value}$$

The MIR coefficient values used were determined based on updated MIR values (2009) by the California Air Resources Board (CARB, 2009) [assessed from webpage https://www.arb.ca.gov/regact/2009 on 17082018].

3. Results & Discussion

3.1 Level of daytime VOCs

Levels for every compound were measured during the sampling period and the results are shown in Table 1. Average concentrations during the daytime sampling period were 6.70 ± 1.57 µg/m^3 for isoprene, 9.42 ± 6.15 µg/m^3 for benzene, 35.04 ± 12.60 µg/m^3 for toluene, 11.20 ± 4.17 µg/m^3 for ethylbenzene, 19.19 ± 10.76 µg/m^3 for m,p-xylene and 18.40 ± 8.56 µg/m^3 for o-xylene. Toluene showed the highest levels measured for all sampling days with a range of 6.32 – 67.08 µg/m^3. The lowest concentrations were measured for benzene during the T2 sampling (1/2/18) and the weekend (3/2/2018). Levels for AVOCs for most of the sampling time followed the pattern toluene > m,p-xylene > o-xylene > benzene/ethylbenzene. The highest BTEX levels occurred during T1. As illustrated in Figure 2, average VOC concentrations during T1 and T3 were high compared to T2 (12-2pm), especially during weekdays. The levels of BTEX were high during T1 and T3 due to the rush hour when traffic on the nearby roads was at its heaviest. As reported by Phuc and Kim Oanh [20], high levels of BTEX related to traffic often occur in SEA cities. The average BTEX level (93.25 µg/m^3) found in KL was similar to those reported in other SEA urban cities: Bangkok, Thailand (107.6 µg/m^3); Ho Chi Minh City, Vietnam (98.2 µg/m^3); but lower than Manila, Philippines (275.1 µg/m^3)[21][22][23].

Daytime isoprene levels were in the range 3.05 – 10.52 µg/m^3 (1.21 – 3.87 ppbv) and the levels were found to be slightly lower during the afternoon T3 sampling. The levels were found to be higher than average isoprene concentrations in a forest area (~1.5ppbv) in Borneo, Malaysia but lower than a palm oil plantation area (~4 ppbv) in Tawau, Sabah [24]. Saito et al. [25] also reported daytime isoprene levels in the range 0.3 – 3.0 ppbv in a reserve forest in Negri Sembilan, Malaysia. The isoprene within urban KL might be released by surrounding forest areas and palm plantations on the outskirts of the KL urban area. During the sampling period, the post-northeast monsoon (Jan-Mar) season occurred and possibly transported isoprene emissions from palm plantations in the states of Pahang and Perak. According to Hellen et al. [12], isoprene also can be emitted by traffic.

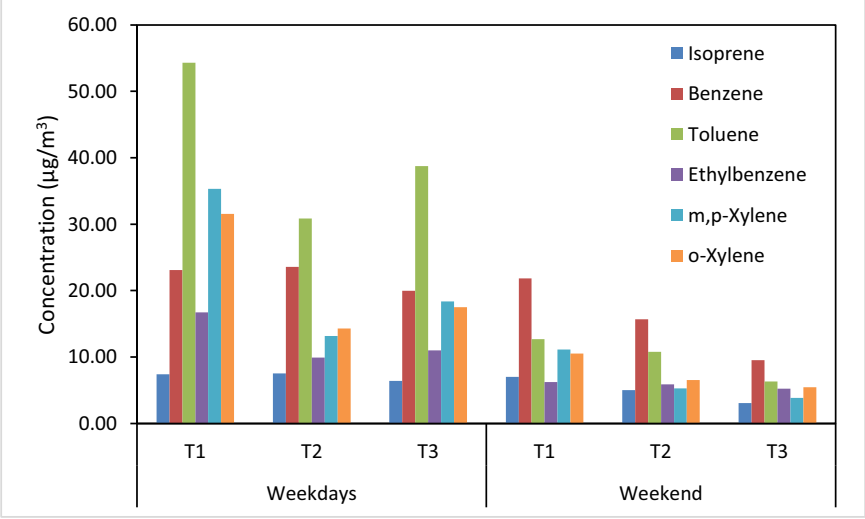

Figure 2. Average concentrations (µg/m^3) of isoprene and BTEX during weekdays and the weekend

3.2 Ozone Formation Potential

The measured levels of VOCs were used to calculate the ozone formation potential (OFP) as shown in Table 2. The range of ∑OFP for the studied VOCs during the sampling period was 218.6 – 733.8 µg/m3. Average OFPs produced by individual compounds were led by m,p-xylene (145.8 µg/m^3) and followed by o-xylene (139.9 µg/m^3), toluene (135.9 µg/m^3), isoprene (71.5 µg/m^3), ethylbenzene (32.8 µg/m^3) and benzene (6.50 µg/m^3). The dominant contributors to OFP in KL were m,p-xylene, o-xylene and toluene and benzene was the lowest due to its low reactivity. The highest OFP occurred on 30/1/2018 and the lowest (218.6 µg/m^3) was measured on the weekend of 3/2/2018. The contribution of isoprene to ∑OFP was calculated as >10% in the KL ambient air and the level increased to 24.5% during the weekend. In this study, AVOCs showed more effects on the local tropospheric ozone in the urban atmosphere. The results for OFP indicated that AVOCs and BVOC have significant impacts on surface ozone in urban KL.

4. Conclusion

Levels of anthropogenic (BTEX) and biogenic (isoprene) VOCs in the ambient air of urban KL during the daytime were determined in this study. ΣBTEX and isoprene averages during the sampling period were 93.25 ± 42.26 µg/m^3 and 6.70 ± 1.57 µg/m^3, respectively. The morning T1 weekday rush hour showed higher BTEX compounds emitted to the air compared to the afternoon T3 and T2. The results clearly can be explained by the volume of vehicles releasing BTEX during incomplete engine fuel combustion. Biogenic isoprene in urban KL was slightly higher compared to forest areas but lower than palm plantation areas. Isoprene in KL was assumed emitted by surrounding palm plantation areas on the outskirts of KL. Both BTEX and isoprene are also ozone precursors that contributed significant OFP. AVOC was found dominant the OFP in the KL urban area, suggesting the impact of anthropogenic activities especially vehicles to the formation of tropospheric ozone.

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Table 1. Concentration (µg/m^3) of isoprene and BTEX during 5 days sampling T1, T2 and T3 in sampling site.

	30/1/2018 (Tue)			31/1/2018 (Wed)			1/2/2018 (Thu)			2/2/2018 (Fri)			3/2/2018 (Sat)		
Compound	T1	T2	T3	T1	T2	T3	T1	T2	T3	T1	T2	T3	T1	T2	T3
Isoprene	10.52	7.32	7.10	6.79	6.87	5.81	9.02	8.46	6.72	3.28	7.57	5.97	7.00	5.02	3.05
Benzene	25.42	9.23	7.13	12.39	5.43	6.80	17.71	2.58	11.41	20.71	9.83	3.11	3.85	3.00	2.76
Toluene	67.08	42.23	43.72	38.45	26.91	36.94	55.59	16.62	53.50	56.13	37.68	20.90	12.71	10.78	6.32
Ethylbenzene	19.30	13.52	11.95	10.61	7.31	9.56	16.41	5.84	18.13	20.60	13.06	4.32	6.23	5.88	5.22
m,p Xylene	46.14	17.74	17.67	24.09	7.79	12.39	36.41	9.87	29.96	34.68	17.35	13.46	11.14	5.29	3.86
o-Xylene	39.47	17.63	18.40	22.37	12.15	15.03	31.86	9.01	25.09	32.57	18.47	11.47	10.52	6.52	5.48

Table 2. MIR value, daytime average concentration and OFP value during sampling period

		30/1/2018 (Tue)		31/1/2018 (Wed)		1/2/2018 (Thu)		2/2/2018 (Fri)		3/2/2018 (Sat)	
Compound	MIR	µg/m^3	OFP	µg/m^3	OFP	µg/m^3	OFP	µg/m^3	OFP	µg/m^3	OFP
Isoprene	10.68	8.31	88.78	6.49	69.31	8.06	86.13	5.61	59.89	5.03	53.68
Benzene	0.69	13.93	9.61	8.21	5.66	10.57	7.29	11.22	7.74	3.20	2.21
Toluene	3.88	51.01	197.92	34.10	132.30	41.90	162.58	38.24	148.36	9.94	38.57
Ethylbenzene	2.93	14.92	43.73	9.16	26.83	13.46	39.44	12.66	37.10	5.78	16.93
m,p Xylene	7.6	27.18	206.59	14.76	112.17	25.41	193.14	21.83	165.92	6.76	51.38
o-Xylene	7.44	25.17	187.25	16.52	122.87	21.99	163.59	20.83	155.00	7.51	55.86
∑ OFP			733.87		469.14		652.17		574.00		218.61

MIR (Maximum Incremental Reactivity) based on updated value by CARB, 2009
OFP (Ozone Formation Potential) = concentration (µg/m^3) x MIR