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Variation of Volatile Organic Compounds (BTEX) in Urban Area

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Abstract

A study of volatile organic compounds (VOCs) concentration changes in the urban atmosphere of Bangkok during January to February 2023 measured four types of VOCs: benzene, toluene, ethylbenzene, and m,p-xylene. VOC concentrations were analyzed every 30 minutes continuously for 24 hours using a gas chromatography with flame ionization detector (GC-FID) at a height of 30 meters above ground level on the rooftop of Faculty of Environment building at Kasetsart University. The results showed that toluene levels were high on haze days. The study of VOCs variation on haze day found that toluene dominated the BTEX profile during haze conditions followed by m,p-xylene, benzene and ethylbenzene, whereas during clear days, ethylbenzene showed the highest concentration, suggesting different emission patterns and atmospheric processes. The diurnal variation analysis between day and night periods during haze conditions, daytime concentrations showed morning peaks (7:00 - 9:00 AM) for all BTEX compounds, with toluene average 5.46 ± 1.11 µg/m³. Night-time levels were generally higher, with toluene reaching 8.06 ± 1.21 µg/m³, indicating pollutant accumulation under atmospheric conditions. The toluene/benzene (T/B) ratio analysis provided crucial insights into emission sources, higher T/B ratios (> 4.0) during haze day, particularly at night, indicated contributions from non-vehicular sources. While on clear day lower T/B ratios suggested vehicular emissions as the predominant source. The study revealed distinct temporal variations in VOC formation pathways between day and night periods during haze episodes. During daytime hours, photochemical oxidation dominated the formation processes. In contrast, nighttime chemistry was primarily driven by NO_3 radical reactions.

Keywords: Volatile Organic Compounds; BTEX; Vehicle exhaust

1. Introduction

The presence of volatile organic compounds (VOCs), particularly BTEX (benzene, toluene, ethylbenzene, and xylenes; BTEX) compounds in urban environments represents a significant environmental and public health concern. Bangkok, Thailand's capital and largest city, faces substantial challenges regarding air quality due to its rapid urbanization, dense traffic conditions, and industrial activities. BTEX compounds, primarily emitted from vehicular exhaust, industrial processes, and evaporation of petroleum products, have garnered increasing attention due to their potential adverse health effects ranging from respiratory irritation to carcinogenic properties (Atkinson *et al.,* 2014).

The overall situation in Thailand for the year 2023 shows that monitoring points in general areas of Pathum Thani Province, Chiang Mai Province, Songkhla Province, Ang Thong Province, and roadside areas in Chiang Mai Province, Khon Kaen Province, and Ang Thong Province had volatile organic compound levels in the atmosphere that met the established standards. However, at monitoring points in roadside areas and general areas of Bangkok, benzene levels were found to exceed the established standards. Similarly, in monitoring points around industrial areas in Rayong Province, benzene, 1,3-butadiene, and 1,2-dichloroethane levels were also found to exceed the established standards. (Pollution Control Department, 2023).

The complex urban landscape of Bangkok, characterized by high-rise buildings, narrow streets, and varying land use patterns, creates unique conditions that influence the distribution and concentration patterns of these airborne pollutants. Understanding the variations of BTEX compounds in Bangkok's urban atmosphere is crucial for effective air quality management and public health protection. This study aims to investigate the concentration patterns and environmental factors affecting BTEX levels in areas of urban Bangkok on haze period.

2. Methodology

2.1 Study area

The experiment was conducted on the rooftop building at Faculty of Environment Kasetsart University, Bangkok, Thailand.

2.2 Field Experimental

A study of volatile organic compounds (VOCs) concentration changes in the urban atmosphere of Bangkok during January to February 2023 measured four types of VOCs: benzene, toluene, ethylbenzene, and m,p-xylene (BTEX). VOCs concentrations were analyzed every 30 minutes continuously for 24 hours using gas chromatography with flame ionization detector (GC-FID) at a height of 30 meters above ground level on the rooftop of the faculty of Environment, Kasetsart University. The O_3, NO, NO_2, NO_x, SO_2 and meteorological parameters including pressure, temperature, humidity in the atmosphere, were all measured by instrument from Thermo Environment Instruments from automatic weather station installed at KU tower at 30 m above the ground (Figure 1).

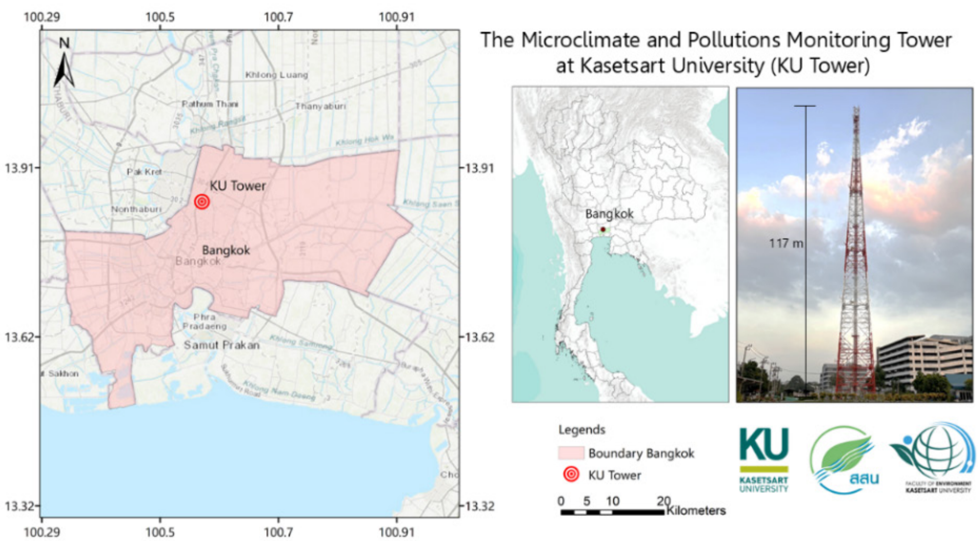

Figure 1. The Microclimate and Pollutions Monitoring Tower at Kasetsart University (KU Tower) (13.854529 N, 100.570012 E).

3. Results and discussion

3.1 Variation of VOCs (BTEX) on haze episode

3.1.1 Variation of VOCs (BTEX) on haze day

The analysis of VOCs (BTEX) concentrations during the 10 day on haze day (haze day is defined as the 24-hour average $PM_{2.5}$ concentration exceed 37.5 μg/m³) revealed distinct patterns, with toluene showing the highest mean concentration (6.69 ± 5.10 μg/m³), followed by m,p-xylene (2.18 ± 2.04 μg/m³), benzene (1.88 ± 1.23μg/m³) and ethylbenzene (1.62 ± 1.14μg/m³) (Figure 2). The synchronized variations in BTEX compounds, particularly between ethylbenzene and m,p-xylene, indicated common emission sources and similar atmospheric conditions, while the substantial day-to-day variations in concentrations (especially evident in toluene's range of 0.25 - 13.98 μg/m³) suggested the influence of varying emission intensities and meteorological conditions during the haze day.

3.1.2 Variation of VOCs (BTEX) on clear day

The VOCs (BTEX) concentrations during the 20 day on clear day in January 2023 exhibited lower levels compared to haze days. Clear day is defined as the 24-hour average $PM_{2.5}$ concentration not exceed 37.5 μg/m³. The results revealed that ethylbenzene showing the highest mean concentration (0.52 ± 0.54 μg/m³), followed by toluene (0.36 ± 0.29 μg/m³), m,p-xylene (0.30 ± 0.44 μg/m³) and benzene (0.10 ± 0.10 μg/m³) respectively. The highest individual concentrations were observed on January 3rd and 4th,

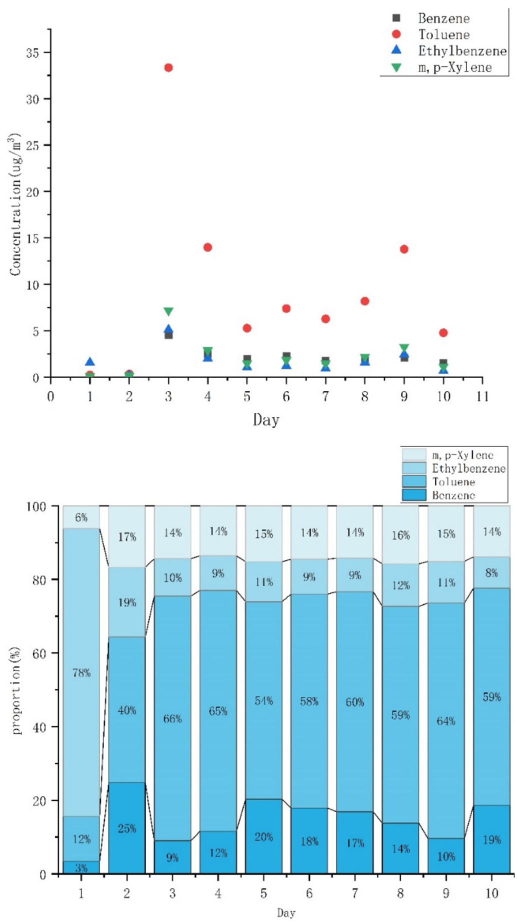

Figure 2. Haze day concentration and proportion of VOCs (BTEX) on the rooftop of Faculty of Environment building, Kasetsart University during January - February 2023.

with peak values for ethylbenzene (2.02 µg/m³), m,p-xylene (1.98 µg/m³), and toluene (1.41 µg/m³), while the lowest concentrations were generally observed in the latter half of the month (Figure 3). Ethylbenzene exhibited the most variable concentrations (range 0.04 - 2.02 µg/m³), contrary to the toluene dominance observed during haze days, suggesting different emission patterns and better atmospheric dispersion conditions during clear days. The consistently lower concentrations of all BTEX compounds during clear days (approximately 5-26 times lower than during haze day) indicate the significant impact of meteorological conditions on pollutant accumulation and dispersion in the urban atmosphere.

3.2 Daytime variation of VOCs (BTEX) on haze day

During daytime among BTEX compounds, toluene showed the highest average concentration of 5.46 ± 1.11 µg/m³, followed by benzene (1.28 ± 0.40 µg/m³), m,p-xylene (1.09 ± 0.47 µg/m³) and ethylbenzene (0.99 ± 0.21 µg/m³) respectivly, with all BTEX compounds showing peak concentrations during morning hours 7:00 - 9:00 AM, likely due to morning traffic. The ratio of toluene to benzene (T/B) on day time was 4.45 indicate that other source besides vehicle emission. (Hui *et al.,* 2019). Ozone (O_3) levels average concentration was 27.37 ppb. Highest concentration of O_3 was 41.62 ppb at 4:00 PM clear increasing trend during daylight, while NO_x average 14.63 ppb

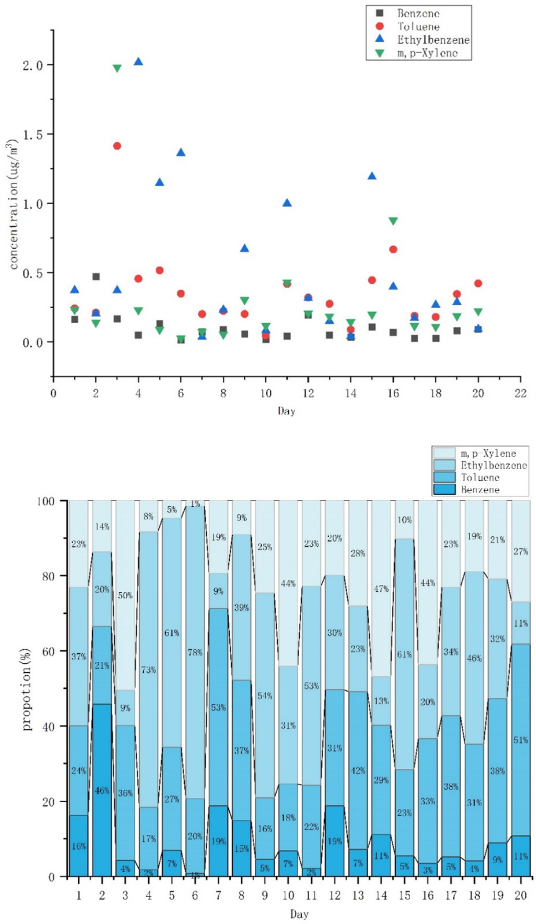

Figure 3. Clear day concentration and proportion of VOCs (BTEX) on the rooftop of Faculty of Environment building, Kasetsart University during January - February 2023.

with higher concentrations during morning hours (Figure 4). The data pattern suggests strong influence from vehicular emissions during morning rush hours, with O_3 showing an inverse relationship to other pollutants, increasing during peak strong solar radiation hours while others pollutants decreased.

The statistical correlations between ozone (O_3) and other pollutants. The data shows significant strong negative correlation between O_3 and NO_x. The NO_x shows the strong negative correlation with O_3 (r = - 0.657, p < 0.01), indicating a strong inverse relationship. This means as NO_x concentrations decrease, O_3 levels tend to increase significantly. The strong negative correlation with NOx suggests photochemical O_3 formation, where NO_x is consumed in the process of O_3 production. O_3 shows moderate weak negative correlations with BTEX compounds; m,p-xylene r = - 0.396 (p < 0.01), benzene r = - 0.267 (p < 0.01), ethylbenzene r = - 0.211 (p < 0.05) and toluene r = - 0.204 (p < 0.01). BTEX compounds don't react directly with O_3, but BTEX compounds contribute to NO_2 formation (Atkinson & Arey, 2003), which is a precursor for O_3 this process requires uv-light, explaining diurnal variation patterns.

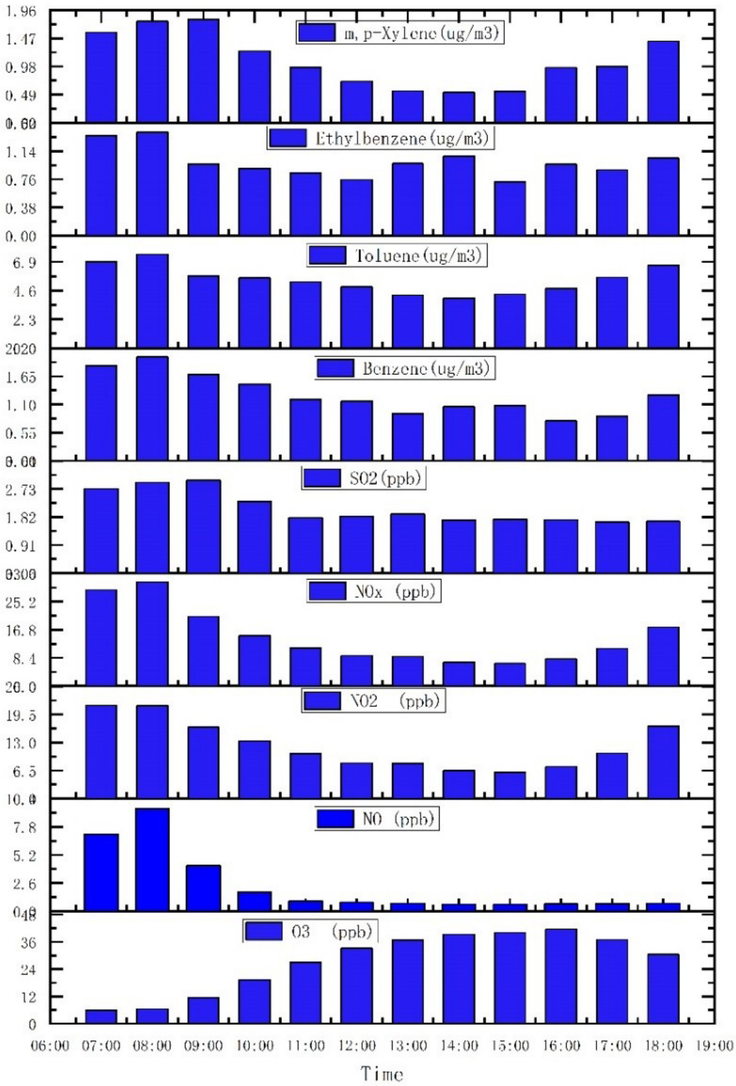

Figure 4. Daytime concentration of VOCs (BTEX), O_3, NO_x and SO_2 on the rooftop of Faculty of Environment building, Kasetsart University during January - February 2023 (haze day).

Table 1. show the statistical correlations on day time between ozone (O_3) and meteorological parameters (relative humidity and temperature) found that O_3 and relative humidity (RH) shows a strong negative correlation (r = - 0.774, $p < 0.01$), indicates that as relative humidity increases, ozone levels tend to decrease significantly. This relationship can be explained by higher humidity reduce photochemical reactions that produce ozone. Because of humidity conditions often associated with cloud cover, which reduces solar radiation needed for ozone formation. The statistical correlations between ozone (O_3) and temperature shows a strong positive correlation (r = 0.878, $p < 0.01$) indicates that as temperature increases, ozone levels also increase significantly, higher temperatures (stronger solar radiation) accelerate photochemical reactions that produce ozone.

3.3 Night-time variation of VOCs (BTEX) on haze day

During night-time hours under haze conditions, among BTEX compounds, toluene demonstrated the highest average concentrations was 8.06 ± 1.21 µg/m³, followed by m,p-xylene (2.17 ± 0.47 µg/m³), benzene (1.87 ± 0.14 µg/m³) and ethylbenzene (1.42 ± 0.30 µg/m³) respectively (Figure 5). This pattern aligns with findings from similar urban studies where toluene typically dominates nighttime VOC profiles (Liu *et al.,* 2019). The ratio of toluene to benzene (T/B) during night-time remained above 4.0, suggesting contributions from sources beyond vehicle emissions, as ratios above 3.0 typically indicate multiple emission sources (Hui *et al.,* 2019). This higher T/B ratio during night-time hours is consistent with findings from other urban areas experiencing haze conditions (Zhang *et al.,* 2021).

NO_x concentrations showed an inverse relationship with O_3 levels during nighttime hours, with NO_x maintaining relatively high concentrations (average 22.44 ± 5.45 ppb) while O_3 levels decreased significantly. This pattern can be attributed to absence of photochemical O_3 production during nighttime. The nighttime accumulation of BTEX compounds was influenced by several meteorological factors such as reduced planetary boundary layer height and absence of photochemical degradation processes, these conditions typically lead to the accumulation of primary pollutants near ground level (Seinfeld and Pandis, 2016).

The statistical analysis of correlations between O_3 and NO_x showed the strongest negative correlation with NO (r = - 0.611, $p < 0.01$), a moderate negative correlation with NOx (r = - 0.317, $p < 0.01$) and weak negative correlation with NO_2 (r = - 0.235, $p < 0.05$) (Table 2). These negative correlations can be attributed to nighttime titration of O_3 by NO forming NO_2 and absence of photochemical O_3 production. The correlations between O_3 and BTEX compounds show weak negative correlation with toluene (r = - 0.243, $p < 0.05$) and non-significant negative correlations with benzene, ethylbenzene and m,p-xylene. The weak correlations suggest limited direct chemical interactions between O_3 and BTEX during nighttime. While the statistical analysis of correlations between NO_2 and VOCs (BTEX compounds) during night-time revealed strong positive correlations this suggesting nighttime oxidation of VOCs primarily occurs through NO_3 radical reactions (Atkinson and Arey, 2003).

Table 1. Pearson correlation coefficients between BTEX compounds, criteria pollutants, and meteorological parameters on haze day (daytime).

	Benzene	Toluene	Ethylbenzene	m,p -Xylene	NO_2	NO_x	O_3	RH	Temp
Benzene	1	0.758**	0.600**	0.777**	0.579**	0.476**	-0.267**	0.546**	-0.157
Toluene	0.758**	1	0.755**	0.792**	0.661**	0.573**	-0.204*	0.356**	0.018
Ethylbenzene	0.600**	0.755**	1	0.613**	0.503**	0.470**	-0.211*	0.323**	-0.020
m,p-Xylene	0.777**	0.792**	0.613**	1	0.677**	0.546**	-0.396**	0.567**	-0.168
NO_2	0.579**	0.661**	0.503**	0.677**	1	0.954**	-0.614**	0.617**	-0.471**
NO_x	0.476**	0.573**	0.470**	0.546**	0.954**	1	-0.657**	0.593**	-0.553**
O_3	-0.267**	-0.204*	-0.211*	-0.396**	-0.614**	-0.657**	1	-0.774**	0.878**
RH	0.546**	0.356**	0.323**	0.567**	0.617**	0.593**	-0.774**	1	-0.768**
Temp	-0.157	0.018	-0.020	-0.168	-0.471**	-0.553**	0.878**	-0.768**	1

**p* value < 0.05, ***p* value < 0.01

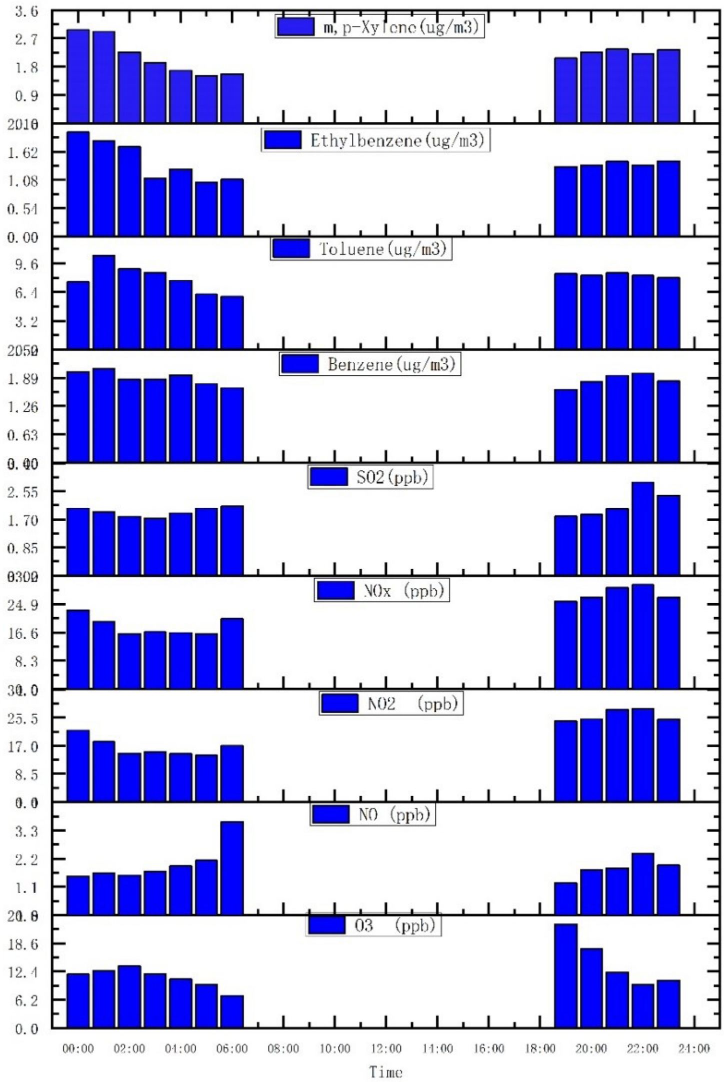

Figure 5. Night-time concentration of VOCs (BTEX), O_3, NO_x and SO_2 on the rooftop of Faculty of Environment building, Kasetsart University during January - February 2023 (on haze day).

Table 2. Pearson correlation coefficients (r) between BTEX compounds, criteria pollutants, and meteorological parameters on haze day (night-time)

	Benzene	Toluene	Ethylbenzene	m,p-Xylene	NO_2	NO_x	O_3	RH	Temp
Benzene	1	0.827**	0.776**	0.836**	0.591**	0.558**	-0.183	0.093	0.280**
Toluene	0.827**	1	0.930**	0.962**	0.698**	0.681**	-0.243*	-0.075	0.363**
Ethylbenzene	0.776**	0.930**	1	0.951**	0.697**	0.663**	-0.155	-0.005	0.236*
m,p-Xylene	0.836**	0.962**	0.951**	1	0.710**	0.682**	-0.170	0.103	0.236*
NO_2	0.591**	0.698**	0.697**	0.710**	1	0.989**	-0.235*	0.040	-0.028
NO_x	0.558**	0.681**	0.663**	0.682**	0.989**	1	-0.317**	-0.001	-0.011
O_3	-0.183	-0.243*	-0.155	-0.170	-.235*	-.317**	1	0.131	-0.107
RH	0.093	-0.075	-0.005	0.103	.040	-.001	0.131	1	-0.517**
Temp	0.280**	0.363**	0.236*	0.236*	-.028	-.011	-0.107	-0.517**	1

*p value < 0.05, **p value < 0.01

4. Conclusion

The investigation of BTEX variations during haze periods revealed distinct patterns of pollutant behavior and concentration changes between haze and clear days. During haze episodes, elevated BTEX concentrations were observed compared to clear days, with mean concentrations approximately 5-26 times higher. Toluene dominated the BTEX profile during haze conditions (6.69 ± 5.10 µg/m³), followed by m,p-xylene (2.18 ± 2.04 µg/m³), benzene (1.88 ± 1.23 µg/m³), and ethylbenzene (1.62 ± 1.14 µg/m³), whereas during clear days, ethylbenzene showed the highest concentration, suggesting different emission patterns and atmospheric processes. The diurnal variation analysis revealed distinct patterns between day and night periods during haze conditions, daytime concentrations showed morning peaks (7:00 - 9:00 AM) for all BTEX compounds, with toluene averaging 5.46 ± 1.11 µg/m³. Night-time levels were generally higher, with toluene reaching 8.06 ± 1.21 µg/m³, indicating pollutant accumulation under atmospheric conditions. The toluene/benzene (T/B) ratio analysis provided crucial insights into emission sources, higher T/B ratios (> 4.0) during haze day, particularly at night, indicated contributions from non-vehicular sources. While lower T/B ratios during clear days suggested vehicular emissions as the predominant source. The study revealed distinct temporal variations in VOC formation pathways between day and night periods during haze episodes. During daytime hours, photochemical oxidation dominated the formation processes, evidenced by strong negative correlations between O_3 and NO_x ($r = -0.657$, $p < 0.01$) and the presence of peak O_3 concentrations (41.62 ppb) during periods of maximum solar radiation. In contrast, nighttime chemistry was primarily driven by NO_3 radical reactions, as indicated by strong positive correlations between BTEX compounds and NO_2 ($r = 0.698 - 0.710$, $p < 0.01$) with decreased O_3 levels. These distinct formation pathways between day and night periods suggest the need for temporally targeted control strategies that address both photochemical oxidation during daylight hours and NO_3 radical chemistry during nighttime, particularly focusing on NO_x and VOC emission reductions during their respective peak formation periods.

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