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Does Light Pollution Affect Nighttime Ground-Level Ozone Concentrations?

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Abstract: Ground-level ozone (O_3) is mainly produced during daytime in the presence of ultraviolet (UV) light and later destroyed by nitrogen oxides during nighttime. However, light pollution caused by the excessive use of artificial lights may disrupt the chemistry of night-time ground-level O_3 by providing enough energy to initiate nighttime ground-level O_3 production. In this study, nighttime (7 p.m. to 7 a.m.) ground-level O_3, nitrogen oxide (NO), and nitrogen dioxides (NO_2) concentrations were observed for three years (2013, 2014, and 2015). The existence of O_3 was found during nighttime, especially in urban areas with a concentration range of 8–20 ppb. The results suggested that nighttime variations of ground-level O_3 concentrations were higher in urban areas than in suburban areas. The mean nighttime O_3 concentration at urban sites varied, possibly because the distribution of anthropogenic lights around the urban sites is brighter than in suburban locations, as indicated by the data from the light-pollution map. This anthropogenic light has not caused the suspected nighttime photolysis processes, which directly slowed nighttime oxidation. The photochemistry rate of J_{NO_2}/k_3 was supposed to be near zero because of the absence of photochemical reactions at night. However, the minimum concentration in all urban and suburban sites ranged from 2–3 ppb, indicating that O_3 might also form at night, albeit not due to light pollution.

Keywords: anthropogenic source; light intensity; light source; nighttime chemistry; troposphere ozone

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1. Introduction

Artificial light has become an essential part of modern civilisation in everyday life and culture because of industrialisation and modernisation [1]. Streets, roads, bridges, airports, commercial and industrial buildings, parking lots, sports centres, and homes are artificial light sources [2]. The use of artificial lights directly degrades natural light in the environment because the former adversely affects not only the health of humans [3], animals, and ecosystems, especially nocturnal wildlife, but also the quality of the sky and air [4]. Stark et al. [4] indicated that street lights are dimmer than the sun and up to 25 times brighter than the full moon.

Ground-level ozone (O_3) exists as one of the secondary air pollutants in the atmosphere and is listed as one of the vital air pollutants affecting Malaysia's air quality [5]. The toxicity of O_3 may affect human health and vegetation [6] Chemically, O_3 formation is induced by ultraviolet (UV) light in the presence of its precursors, such as nitrogen oxides (NO_x) and volatile organic compounds (VOCs) [7,8], and this daytime reaction is called a photochemical reaction. In addition to the variability of its precursors, UV intensities

and meteorological factors influence O_3 formation [3]. During the day, ground-level O_3 formation is usually related to hydroxyl radical (OH) chemistry. OH is inherently linked to the chemistry of nitric oxide (NO) and nitrogen dioxides (NO_2); meanwhile, at night, nitrate radical (NO_3) serves as a night-time oxidant [9,10].

O_3 transformation during daytime and nighttime should be extensively explored. Previous measurement and modelling studies have investigated the effects of anthropogenic sources on diurnal variation during daytime and nighttime [11–13]. Overall, variations in O_3 at night have been studied, and the possible factors that contribute to the presence of O_3 at night have been analysed [14–18]. Nighttime O_3 variations are attributed to the weakening of vertical mixing at night [18] and the effects of emissions and meteorological factors [14–16,19,20].

Yan et al. [18] observed the O_3 variability over 1000 US sites from 1990 to 2014 and found that NO_x reduction led to changes in O_3 concentrations at night because of a decrease in O_3 titration rates. Another oxidant, NO_3, generated at night by the reaction of NO_2 with O_3, directly acts as a cleansing compound because it neutralises some NOx that pollutes daytime air and leads to wheeze-inducing levels of O_3 [21]. NO_3 further reacted with NO_2 to establish a chemical equilibrium with N_2O_5 [22]. However, further research has shown that this nightly cleansing action is not as effective as expected because NO_3 is being destroyed by the light reflected in the sky by outdoor lighting on the ground [4,23]. In the presence of anthropogenic lights, NO_3 is destroyed, and O_3 concentrations increase through possible chemical reactions occurring at night as in reactions (R1) and (R2). Reaction (R1) can occur during daytime; however, NO_3 is quickly photolysed by daylight (R3), and NO_3 and N_2O_5 are heavily suppressed during the day.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R1)}$$

$$NO_3 + NO_2 \Leftrightarrow N_2O_5 \quad \text{(R2)}$$

$$NO_3 + \text{light}(\lambda < 590\text{nm}) \rightarrow NO_2 + O \quad \text{(R3)}$$

Stark et al. [4] revealed that this nighttime phenomenon is related to increasing the number of photons in the atmosphere and directly enhancing O_3 photochemical reactions. Stark et al. [23] also performed aircraft measurements and found that UV intensities from anthropogenic light sources at night enhance O_3 formation in brighter cities. O_3 production is not limited to daytime; this phenomenon likely occurs all day. Nevertheless, the nighttime production rate is very much lower than the daytime photochemical reactions. The loss of NO_3 significantly affects nighttime pollutant levels and next-day O_3 production because light pollution exacerbates due to rapid urbanisation. Demands for light during nighttime will continuously increase in the future because more locations are being transformed into urbanised cities, where nighttime light intensities are higher. Thus, this study intended to critically investigate the possible relationship between nighttime light pollution and ground-level O_3 variations in urban and suburban areas in Malaysia. Differences in light intensities in urban and suburban areas are crucial to this study to establish the possible impact of light pollution on nighttime O_3 concentrations.

2. Materials and Methods

2.1. Light Pollution in Urban and Sub-Urban Areas

Specific sites in urban and suburban areas were selected to compare their nighttime O_3 concentrations. Putrajaya (PT), Seremban (SB), and Bandaraya Melaka (BM) were chosen as representatives of urban sites. These sites were situated in the cities where the population density was higher than that of suburban sites, i.e., Muar (MR), Indera Mahkota (IM), and Tanjung Malim (TM). A city is considered a significant contributor to light pollution because of more artificial light sources, such as street lights, security lights, lights on vehicles, and lighted buildings and towers that vary to many degrees [1,24].

Figure 1 illustrates the irradiance map of peninsular Malaysia. Table 1 depicts the Bortle dark-sky scale [25], artificial brightness (artificial lights that increase the night sky

luminance), and brightness (natural brightness of the night sky) recorded at different location profiles by referring to a light-pollution map [26]. Amongst the selected sites, PT had the highest artificial brightness (6350 μcd/m^2) and brightness (6520 μcd/m^2). It was classified as class 8–9, a city sky by the Bortle dark-sky scale. The lowest artificial brightness and brightness were recorded at the TM site, representing the suburban site with 713 and 884 μcd/m^2, respectively. TM was classified as class 5 (suburban sky) based on the Bortle dark-sky scale.

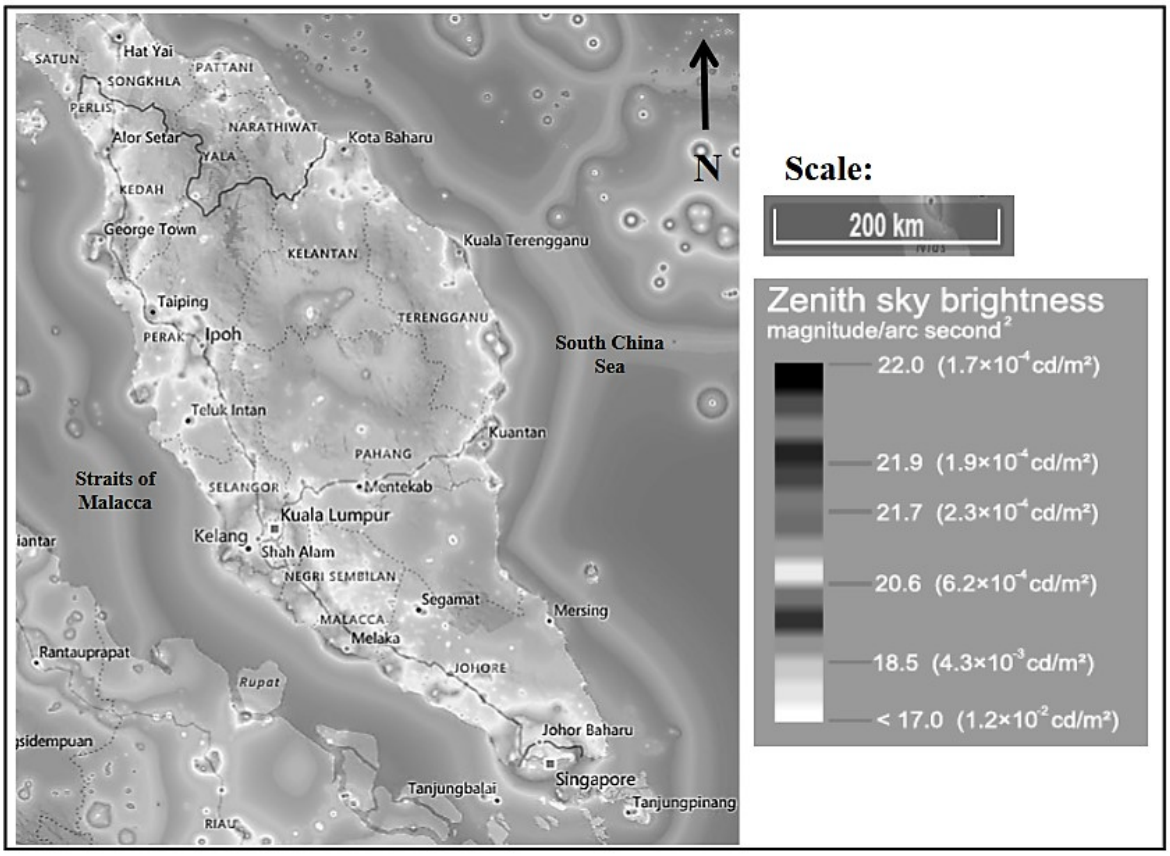

Figure 1. Irradiance map of Peninsular Malaysia [26].

Table 1. Description of the location, population, and brightness of the selected sampling sites.

Group	Station	Station ID	Coordinate (°)	Population [27]	* Bortle Dark-Sky Scale	** Artificial Brightness (μcd/m^2)	** Brightness (μcd/m^2)
Urban	Putrajaya	PT	N 2.9263 E 101.6964	90,000	8–9 (City sky)	6350	6520
	Seremban	SB	N 2.7267 E 101.9368	372,917	7 (Sub-urban)	4960	5130
	Bandaraya Melaka	BM	N 2.1243 E 102.1411	180,671	7 (Sub-urban)	4200	4380
Sub-urban	Muar	MR	N 2.0599 E 102.5951	127,897	6 (Bright Sub-urban)	2160	2230
	Indera Mahkota	IM	N 3.8207 E 103.2970	64,343	6 (Bright Sub-urban)	2510	2680
	Tanjung Malim	TM	N 3.6850 E 101.5241	60,791	5 (Sub-urban)	713	884

* Referring to Bortle [25]; ** referring to light-pollution map [26].

2.2. Nighttime Data Collection

The secondary data in 2013, 2014, and 2015 were used in this study and obtained from the Department of Environment, Malaysia [28]. For O_3 data collection, the UV absorption O_3 analyzer Model 400A was used together with the Analyzer Model 200A for NO and NO_2 data collection. NO_3 concentration was not monitored at the DOE stations, so the results depended on the recorded O_3, NO, and NO_2 concentrations. The secondary data were recorded for 24 h (12.00 a.m.–12.00 a.m.) consecutively for 3 years. The data were grouped as daytime (7 a.m. to 7 p.m.) and nighttime (7 p.m. to 7 a.m.) to differentiate between daytime and nighttime analysis. The secondary data's quality control and quality assurance were carried out properly according to the standard [29]. Table 2 shows the details of the monitoring instruments, monitoring periods, and total durations to collect the data on O_3, NO, and NO_2 concentrations.

Table 2. Summary of data collection information.

Type of Data	Secondary Data	References
Instrument	UV Absorption O_3 Analyzer Model 400A $NO/NO_2/NO_x$ Analyzer Model 200A	[28–31]
Monitoring period	12.00 a.m.–12.00 a.m.	
Total duration	24 h	

2.3. Nighttime Chemistry and O_3 Formation

Clapp and Jenkin [22] revealed a point where NO_2 is destroyed and reproduced fast to maintain a cycle. The rate of NO_2 photolysis (photolyis, J_{NO_2}) as a coefficient of the reaction of NO with O_3 (k_3) was calculated using Equation (1) to determine the variations in O_3 production rates during daytime and nighttime [21,22].

$$\frac{J_{NO_2}}{k_3} = \frac{[O_3][NO]}{[NO_2]} \quad (1)$$

This result provided the value of O_3 production and destruction during daytime and nighttime.

3. Results

3.1. Hourly Diurnal Variation in Urban and Suburban Area

Table 3 shows the descriptive statistics of O_3, NO_2, and NO at urban and sub-urban sites. Meanwhile, the mean concentrations for O_3, NO_2, and NO at urban and suburban sites are illustrated in Figure 2. The highest daytime and nighttime mean O_3, NO_2, and NO concentrations were recorded in urban areas compared to sub-urban areas. The highest is PT (for 2013, O_3: 41.69 ± 25.49 ppb; NO_2: 9.98 ± 1.98 ppb; and NO: 5.47 ± 4.81 ppb) followed by BM and SB sites. Meanwhile, in sub-urban sites, the highest is MR (for 2013, O_3: 32.26 ± 14.92 ppb; NO_2: 5.66 ± 1.06 ppb; and NO: 7.42 ± 3.41 ppb), followed by IM and TM sites. The high O_3 concentrations in urban sites happen due to various anthropogenic activities, which became a significant source of O_3 precursors [16,30,32,33].

Figures 3 and 4 show the diurnal trend of the mean O_3, NO, and NO_2 concentrations. Nighttime O_3 concentration increased during late afternoon hours (6 p.m. to 7 p.m.), and this observation was similar to Jhun et al. [34]. PT had the highest variation of O_3, NO, and NO_2 because it was located in Malaysia's urban city and federal administrative capital. It is also an intelligent garden city with a well-lit area for night sightseeing activities. TM had the lowest trend of O_3, NO, and NO_2 and represented the suburban site trend. The trend exhibited similarities to previous findings in urban and suburban sites, peaked during daytime (2 p.m.), and decreased during nighttime, but the concentrations differed [14,16,17,35]. Faid et al. [24] investigated the profile of the night sky in Malaysia. They found that population and location distance from a city are the significant variables of light pollution because Kuala Lumpur is five times brighter than Teluk Kemang, a suburban sky.

Table 3. Descriptive statistics of O_3, NO_2, and NO at different sites (mean ± standard deviation).

Site	Time	2013			2014			2015		
		O_3 (ppb)	**NO_2 (ppb)**	**NO (ppb)**	**O_3 (ppb)**	**NO_2 (ppb)**	**NO (ppb)**	**O_3 (ppb)**	**NO_2 (ppb)**	**NO (ppb)**
PT	DT	41.69 ± 25.49	9.98 ± 1.98	5.47 ± 4.81	29.31 ± 19.14	14.15 ± 3.40	9.14 ± 8.31	43.06 ± 24.07	14.72 ± 4.23	6.07 ± 4.88
	NT	20.91 ± 12.40	16.74 ± 4.40	6.02 ± 3.15	8.22 ± 6.52	20.61 ± 3.65	10.95 ± 4.46	18.55 ± 10.21	22.26 ± 3.75	5.21 ± 1.35
SB	DT	35.50 ± 22.05	9.60 ± 2.13	5.05 ± 5.45	32.41 ± 17.11	7.30 ± 3.30	3.20 ± 3.40	21.37 ± 11.22	8.58 ± 2.91	4.16 ± 4.40
	NT	10.76 ± 9.02	15.07 ± 5.26	3.75 ± 1.32	22.43 ± 12.18	11.56 ± 5.11	2.39 ± 1.17	10.94 ± 5.18	11.38 ± 4.25	2.47 ± 0.65
BM	DT	36.31± 16.44	8.40 ± 2.31	4.84 ± 3.02	32.85 ± 13.11	5.58 ± 2.09	2.08 ± 1.04	37.37 ± 18.47	5.93 ± 2.26	4.29 ± 0.97
	NT	19.14 ± 7.82	11.84 ± 2.65	3.14 ± 1.26	23.96 ± 8.34	8.97 ± 4.25	1.84 ± 0.64	23.32 ± 9.54	8.78 ± 2.21	3.18 ± 0.31
MR	DT	32.26 ± 14.92	5.66 ± 1.06	7.42 ± 3.41	Data not available			27.21 ± 12.48	9.27 ± 2.63	4.21 ± 2.23
	NT	17.06 ± 6.54	9.59 ± 2.68	8.67 ± 3.39				16.05 ± 7.11	13.55 ± 2.85	2.99 ± 0.49
IM	DT	25.56 ± 14.94	6.08 ± 2.43	4.68 ± 2.72	26.68 ± 13.79	4.87 ± 2.85	2.73 ± 3.63	Data not available		
	NT	11.22 ± 6.10	10.63 ± 2.88	4.95 ± 3.31	17.61 ± 8.40	6.98 ± 1.84	1.45 ± 0.70			
TM	DT	21.92 ± 13.10	7.61 ± 2.05	3.49 ± 4.39	31.51 ± 21.48	6.53 ± 2.20	3.73 ± 5.20	Data not available		
	NT	9.31 ± 3.79	9.15 ± 5.65	2.76 ± 1.20	13.01 ± 12.13	11.14 ± 2.21	3.61 ± 2.21			

Note: DT is daytime; NT is nighttime.

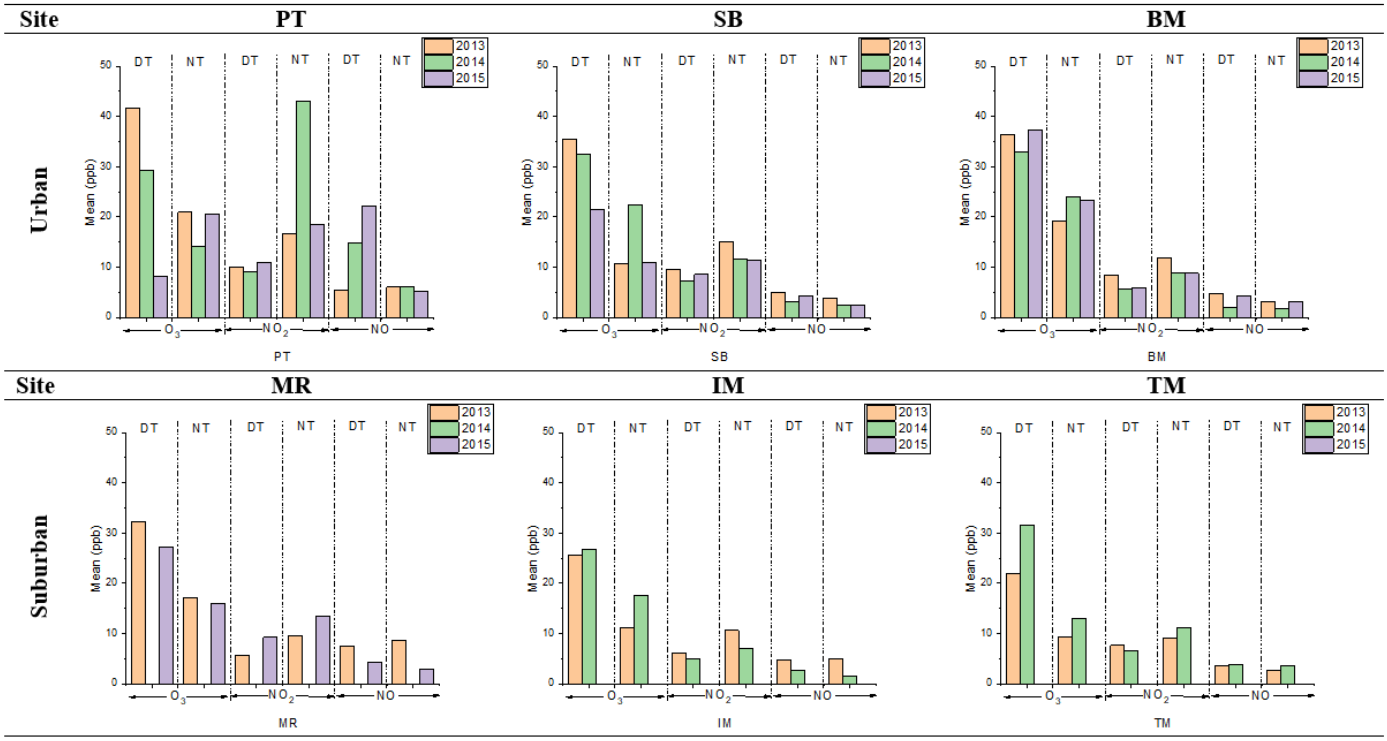

Figure 2. The mean concentrations of O_3, NO_2, and NO, during daytime (DT) and nighttime (NT), at urban and suburban sites in 2013, 2014, and 2015.

The minimum mean O_3 concentration during nighttime did not reach zero, and the value remained stable at 8–20 ppb at an urban site until the following day. In a suburban area, the concentrations were between 8 and 14 ppb. Even though the values were not high, the O_3 concentrations should be at zero during nighttime because of the absence of sunlight. This is due to the decreased hydroxyl radical (as they are produced mainly OH) concentrations from the photolysis of stable molecules, and supposedly no further reaction occurs [16]. HONO photolysis contributes more than 50% of production on average daytime, while nighttime OH production is mainly from the O_3 reactions with alkenes [36]. The radical propagation is efficient due to the abundance of NO in an urban environment, which results in O_3 production. Khan et al. [37] found that NO_3 and OH levels during nighttime were in the range of 0.01 to 10 ppt and 1×10^4 to 1×10^6 molecule cm^{-3}, respectively. The OH and NO_3 concentration variations in different locations depended on the air and tended to be lower in clean air masses and higher in polluted areas (urban areas). A NO_3 radical, another oxidant, is generated during nighttime via the reaction of NO_2 and O_3. NO_3 radicals react with NO_2 to establish a chemical equilibrium with N_2O_5 [38].

Besides anthropogenic sources and O_3 precursors [14–16], mean nighttime O_3 concentrations in urban sites vary because the distribution of anthropogenic lights around the metropolitan area had more brightness than that in the suburban locations. The brightness of light with specific wavelength intensities disturbs the reaction of nocturnal nitrogen oxides (NO_3 and N_2O_5) that have the potential to either remove nitrogen from the atmosphere or store it and then release it during daytime. Even though the effect is small, this parameter is measurable and accounts for 2–3% of the NO_3 loss in some brighter sites Still, this phenomenon has different consequences for O_3 formation [39], where the lighting in urban sites influences NO_3 photolysis as a sink for NO_3 and N_2O_5 at night.

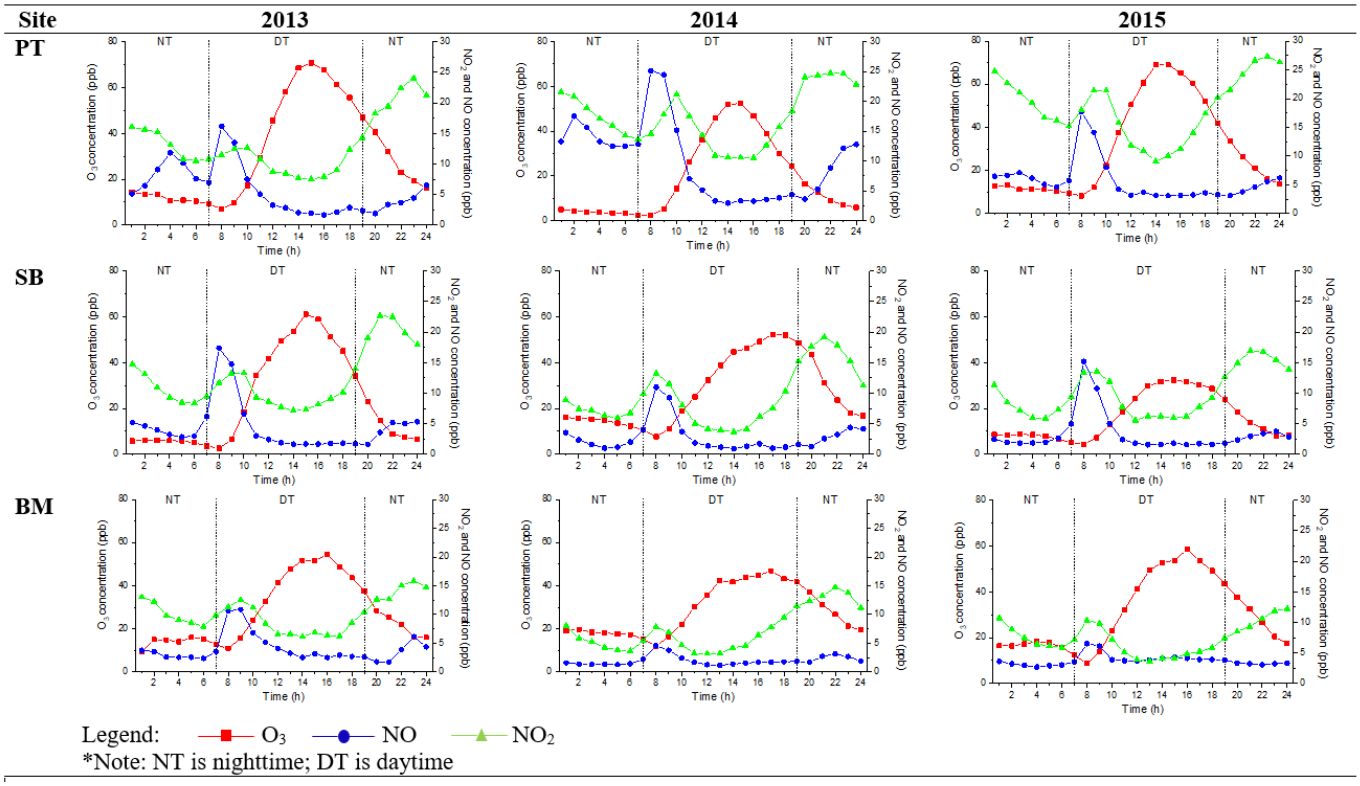

Figure 3. Hourly diurnal plots of O_3, NO_2, and NO, at urban sites (PT, SB, and BM) in 2013, 2014, and 2015.

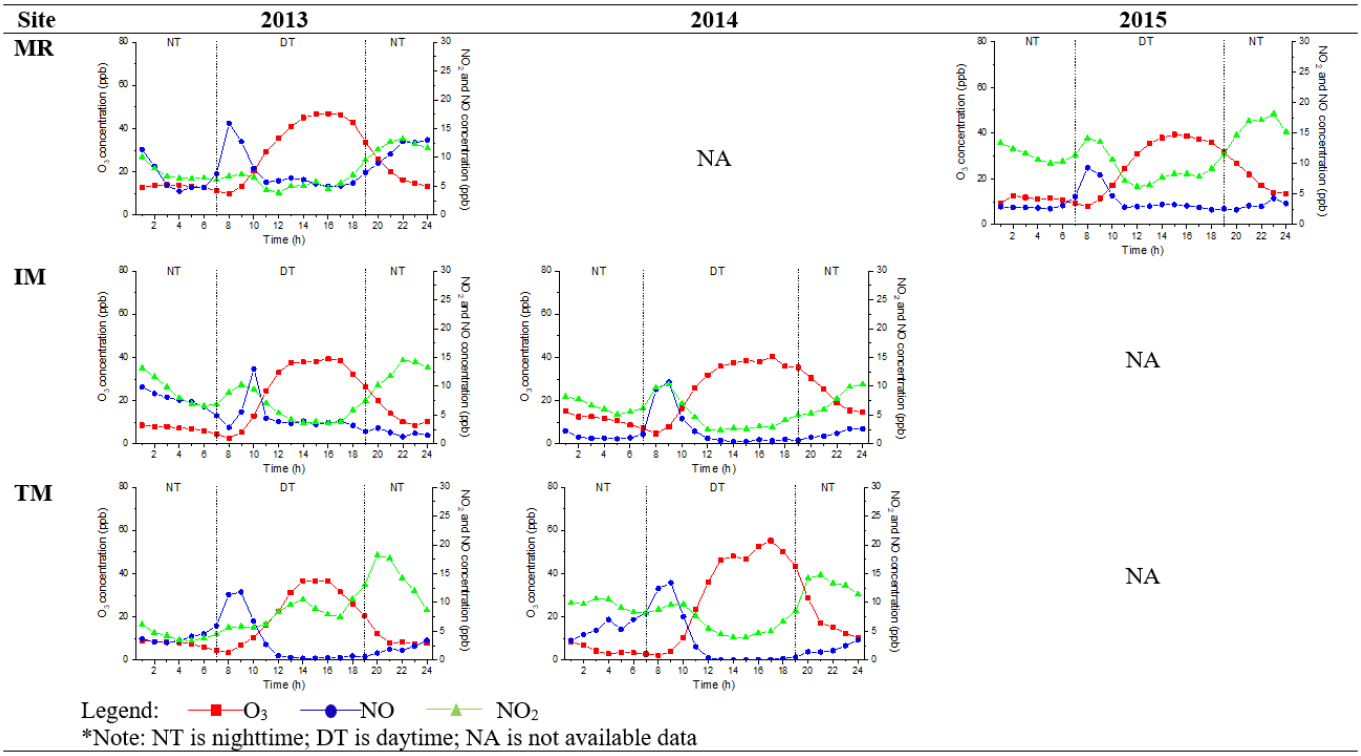

Figure 4. Hourly diurnal plot of O_3, NO_2, and NO, at suburban sites (MR, IM, and TM) in 2013, 2014, and 2015.

3.2. Nighttime Ozone Formation

The photochemistry rates of O_3, NO, and NO_2 concentrations at urban and suburban sites depend on the rate of NO_2 photolysis (J_{NO_2}) and NO titration (k_3), and their reaction rates can be depicted in a timescale over a few minutes [21]. The average diurnal variations in J_{NO_2}/k_3 rates in urban and suburban areas are illustrated in Figure 5. The J_{NO_2}/k_3 shows the average hourly formation of O_3 concentrations. The figure also demonstrates that the diurnal variations in J_{NO_2}/k_3 differ in urban and suburban areas, and this phenomenon is similar to that described by Han et al. [21] in Tianjin, China.

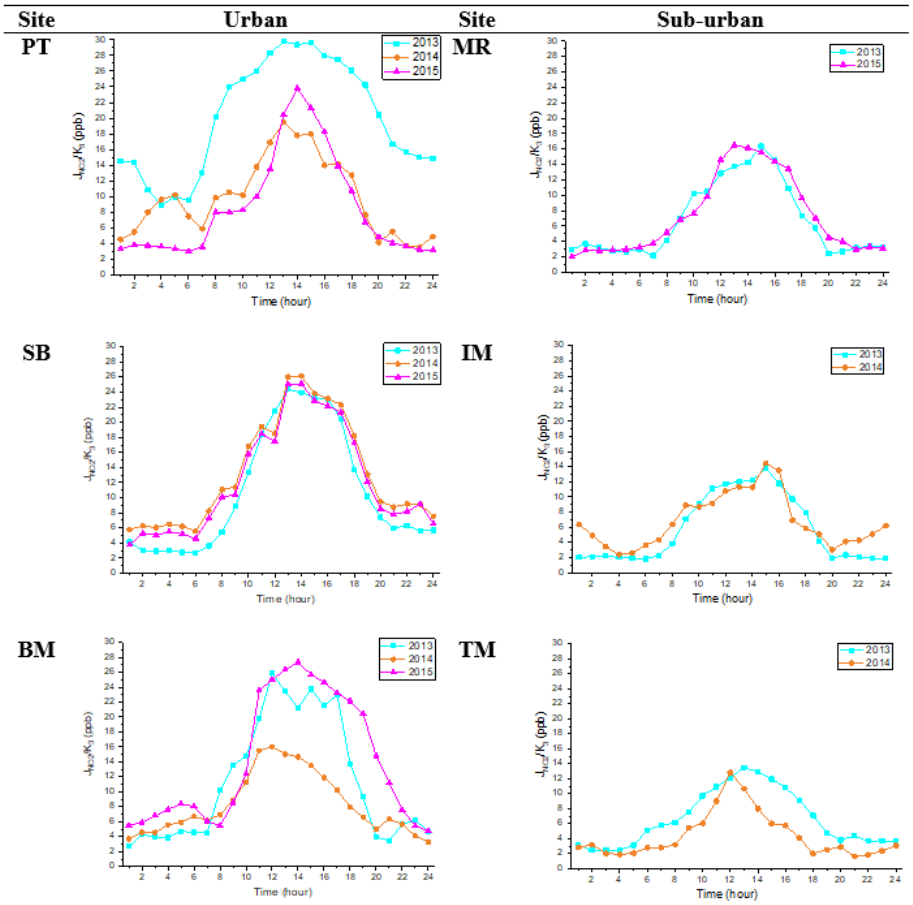

Figure 5. J_{NO_2}/k_3 diurnal plots at urban and suburban sites in 2013, 2014, and 2015.

In urban sites, the O_3 concentrations in SB increased after 11 p.m. Likewise, the O_3 concentrations in BM also increased, but instead the increment was recorded at 9 p.m. In suburban sites (IM and TM), the O_3 production rates increased after 9 p.m. These findings might indicate some light pollution contribution to O_3 formation. Theoretically, during nighttime, the value of J_{NO_2}/k_3 should be zero because of the absence of photochemical reactions. However, the minimum photochemistry rate in all urban and suburban sites was two ppb, indicating that O_3 was also formed at night, even with minimal value. This result tends to be higher than those Awang et al. [40] found in the urban site (0.10 ppb). This difference is due to the variation in the weather parameters, including different locations (urban port cities) and climate. The highest nighttime photochemistry rate was 14.8 ppb, recorded at PT in 2013.

The obtained result showed that during the night, O_3 photochemical reactions failed to stop. Stark et al. [4] stated that nighttime oxidation could be slower due to lights.

Brown et al. [41] also found that nighttime light sources could increase O_3 production during daytime, especially in brighter cities; higher intensities are possible, as seen in Los Angeles.

4. Conclusions

The secondary data in 2013, 2014, and 2015 from the Department of Environment, Malaysia has been used to investigate the possible relationship between nighttime light pollution and ground-level O_3 variations between two sites: urban and sub-urban areas in Malaysia. The data were grouped as daytime (7 a.m. to 7 p.m.) and nighttime (7 p.m. to 7 a.m.) to analyze the variations. An hourly diurnal plot was used to depict the variations during daytime and nighttime. Remarkably, from the results, urban sites (PT) had the highest trend of nighttime O_3, NO, and NO_2 because they were located in the urban area, with mean nighttime O_3 concentrations ranging from 8 ppb to 20 ppb. Urban sites (PT) also had the highest artificial brightness (6350 μcd/m^2) and brightness (6520 μcd/m^2), respectively. The mean nighttime O_3 concentration in urban sites varied, possibly because the distribution of anthropogenic lights around the metropolitan area had more brightness than in suburban locations. Suburban sites (TM) had the lowest trend of O_3, NO, and NO_2, with the mean nighttime concentration ranging from 8 ppb to 14 ppb. However, the minimum J_{NO_2}/k_3 in all urban and suburban sites was two ppb, indicating that O_3 was formed during nighttime. The highest photochemistry rate was 14.8 ppb, recorded in the urban area (PT) in 2013. Thus, O_3 production during daytime could be increased by nighttime light sources, which reduced nighttime cleansing via the destruction of NO_3 radicals.

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