Journal of Sustainability Science and Management
Volume 14 *Number* 5, October 2019: 195-201
ISSN: 1823-8556

NIGHT-TIME GROUND-LEVEL OZONE TRENDS AND VARIABILITY OVER THE URBAN SITES

SYABIHA SHITH* AND NOR AZAM RAMLI

Environmental Assessment and Clean Air Research, School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia, 14300, Nibong Tebal, Penang, Malaysia.

**Corresponding author: syabiha@usm.my*

Abstract: This study evaluates the variation of night-time ground-level ozone (O_3), nitrogen dioxide (NO_2) and nitric oxide (NO) from year 2015 to 2016. During this period, the recorded maximum night-time ground-level O_3 was 55 ppb at Putrajaya (PT), which have more areas with higher brightness level compared to another urban site, Alor Setar (AS) at 21 ppb. Lower NO concentrations restricted the sinking agents, thus, reducing the depletion rates and resulted in O_3 to remain in the atmosphere. The contributor toward night-time ground-level O_3 concentration in the urban site was not only NO_2 concentration, as light pollution might enhance the O_3 formations. The photochemistry rate was commonly accounted to be zero due to the absence of photochemical reactions at night. However, the minimum photochemistry rate in both urban was recorded at the ranged from 1.50-2.70 ppb, indicating that O_3 was also titrated at night even though the value is not as high as during the day.

Keywords: Diurnal variations, nitrogen dioxide, nitric oxide, sustainability, photochemistry.

Introduction

Ground-level ozone (O_3) is a secondary pollutant can arise from in-situ photochemical production resulting from anthropogenic precursor's emissions; a mixture of reactive nitrogen oxides (NO and NO_2), and volatile organic compounds (VOCs) (Duce *et al*., 2008). Previous researchers had found that daytime variation of diurnal ground-level O_3 in urban sites was characterised by higher concentrations during daytime, wherein, showed that production of ground-level O_3 induced by anthropogenic emissions (Alvarez *et al*., 2000; Ghazali *et al*., 2010; Hassan *et al*., 2013; Klein *et al*., 2019). There are no significant sources of O_3 in the atmosphere other than reaction 1 (R1). The reaction of NO_2 as O_3 precursor is limited, only occurred with the presence of sunlight, *hv* (wavelengths <424 nm) (R2) (Zhang *et al*., 2004; West *et al*., 2006). Once O_3 were formed, they then readily react with NO to regenerate NO_2 (R3) when no other chemical species are involved.

$$O + O_2(+M) \rightarrow O_3(+M) \quad (R1)$$

$$NO_2 + hv(\lambda<424\ nm) \rightarrow NO + O_2 \quad (R2)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (R3)$$

At night, as the photochemical process ceases, reactions with hydrogen oxide radicals (HO_x), dry deposition and titration with NO will remove O_3. Besides that, O_3 also reacts with NO_2 (R4) to form nitrate radical (NO_3); the NO_3 radical was interconverted with NO_2 and dinitrogen pentoxide (N_2O_5) (R5). The NO_3 and N_2O_5 are destroyed photochemically to reproduce ground-level O_3 when sunlight returns in the next morning (Morris *et al*., 2010; Kulkarni *et al*., 2013; Klein *et al*., 2019). Consequently, the abundance of NO near the ground level leads to the removal of O_3 due to the titration (Zhang *et al*., 2004; West *et al*., 2006).

$$NO_2 + O_3 \rightarrow NO_2 + O_2 \quad (R4)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \quad (R5)$$

Observation over 1000 sites in the United States recorded that NO reduction has led to changes in O_3 concentrations at night because of the increased in O_3 titration rates (Yan *et al*., 2018). NO_3 acts as a cleansing compound as it

neutralises some NO and NO_2 that pollutes the daytime air. Stark *et al*. (2010; 2011) stressed out that this nightly cleansing action is not effective as expected because NO_3 is being destroyed by the light that reflected the sky by outdoor lighting on the ground. In the presence of artificial lights, NO_3 is destroyed, and O_3 concentrations increase through possible chemical reactions occurring at night. If this theory is proven, then O_3 production is not limited to daytime, this phenomenon is likely to occurs all day.

In urban sites, installation of the artificial lights had been a trend, where the possibility of light pollution to the induced formation of ozone could happen. The notion of the photochemical reaction of O_3 does occur only during daytime (with the existence of sunlight), and logically, there is no formation of O_3 could occur at night, hence, could be contested. Thus, this study investigated the variability of O_3 changes during night-time, and explored the possible changes in rates of night-time reactions of O_3, NO_2 and NO.

Materials and Methods

Study Location

In this study, two continuous air quality monitoring stations were selected, which are, Putrajaya (PT) and Alor Setar (AS). Both stations are categorised as urban stations as its located in the city centre with artificial light being installed around the area to provide the 'brightness' during night-time. PT is also known as Federal Territory Putrajaya, a planned city and the federal administrative centre of Malaysia. Meanwhile, AS station lies in the central region of Kedah, one of the most important cities on the west coast of Peninsular Malaysia. PT had higher brightness due to artificial lights compared to the AS site by referring to light pollution map as shown in Table 1 (Light Pollution Map, 2018).

Data Analysis

Hourly measurements of O_3, NO_2, and NO, between 2015 and 2016 were provided by the Department of Environment, Malaysia, for two urban air quality monitoring stations (PT and AS). For each year, all the data were averaged hourly, monthly (January to December) and for annual mean values. In order to differentiate daytime and night-time, daytime was considered as, from 7:00 to 18:00 h local time (GMT +8), while night-time as, 19:00 to 6:00 h local time. Hourly measurement was carried out by using the instrument as shown in Table 2 for every parameter.

Photostationary State of Ground-level Ozone

Equilibrium between O_3, NO_2 and NO referred to as a photo stationary state. The equilibrium was described by Eq. (1) (Seinfeld & Pandis, 2010). Clapp and Jenkin (2001) revealed a point where NO_2 is destroyed and reproduced at a fast rate that maintains a steady-state cycle. The rate of NO_2 photolysis (j_{NO_2}) as a coefficient of the

Table 1: Description of the monitoring stations selected in this study

Station ID	Station Name	Coordinates	Brightness (mcd/m^2)	Artificial Light (µcd/m^2)
PT	Putrajaya	2°55'34.76"N, 101°41'50.63"E	5.800	5630
AS	Alor Setar	6°7'28.90"N, 100°22'4.30"E	2.300	2130

Note: Brightness and artificial light referring to Light Pollution Map (2018)

Table 2: Measurement of O_3, NO_2, and NO provided by the Department of Environment, Malaysia

Parameter	Instrument	Reference
O_3	Model 400E, UV Absorption Ozone Analyser	Ghazali et al. (2010); Mohammed et al. (2013)
NO_2 and NO	Model 200A NO/NO_2 Analyser	Ghazali et al. (2010)

reaction of NO with O_3 (k_3) was calculated to determine the variations in O_3 production rates during daytime and night-time (Clapp & Jenkin 2001, Han *et al*., 2011). The positive differences of j_{NO_2}/k_3 ($\Delta j_{NO_2}/k_3$) rate with previous hour indicating that NO_2 photolysis rates are higher than NO titration rates, while negative indicate that NO_2 photolysis was lower than NO titration (Awang *et al*., 2015).

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

Results and Discussion

Variability of hourly diurnal O_3, NO_2, and NO concentrations in two monitoring stations, PT and AS for two years were illustrated in Figure 1. In general, both stations showed a similar pattern throughout the daytime and night-time, but differed by their concentration levels. The results showed that O_3 concentrations are higher in PT compared to AS, even though both stations were in the urban area. The mean night-time ground-level O_3 concentrations for both sites were 13 ppb. Meanwhile, the maximum hourly O_3 concentrations at these stations were 55 ppb for PT and 21 ppb for AS. Various anthropogenic activities became significant sources of O_3 precursors and contribute to the high O_3 concentrations. These findings is in line with the previous researchers, which found that the most dominant sources were in an urban area (Ghazali *et al*., 2010; Latif *et al*., 2012; Strode *et al*., 2019).Vehicles emissions were getting higher as the vehicles moving in low speed during road congestion thus causes a high concentration of NO releases (Banan *et al*., 2013) and subsequently higher levels of NO_2 production, which is the main precursors of O_3.

The diurnal trend shows higher O_3 concentrations during the daytime as compared to night-time. Daytime and night-time O_3 concentration peak occurred between 14:00 until 15:00 h and 19:00 h, respectively. During daytime, O_3 concentration increase and peak in the afternoon, while getting lower as the NO emission is the highest. At night, O_3 concentrations are much smaller than during the daytime, as expected. These situations happen mostly due to deposition and titration by NO in the stable nocturnal boundary layer (Strode *et al*., 2019). For both stations, depositions of O_3 happen to start from 19:00 until early morning (6:00) with the maximum O_3 concentrations during night-time is 30 ppb recorded at PT. The minimum O_3 concentrations recorded also at PT with 6 ppb at 8:00. Retained concentrations during daytime and O_3 transported from another place could be the factors that make the night-time O_3 recorded at night. Awang *et al*. (2015) and Yan *et al*. (2018) reported that increasing trends in night-time O_3 due to decreases in NO, which restricted the sinking agents to remain in the atmosphere.

As regards to the photo stationary state, even the production rate at night was not as much

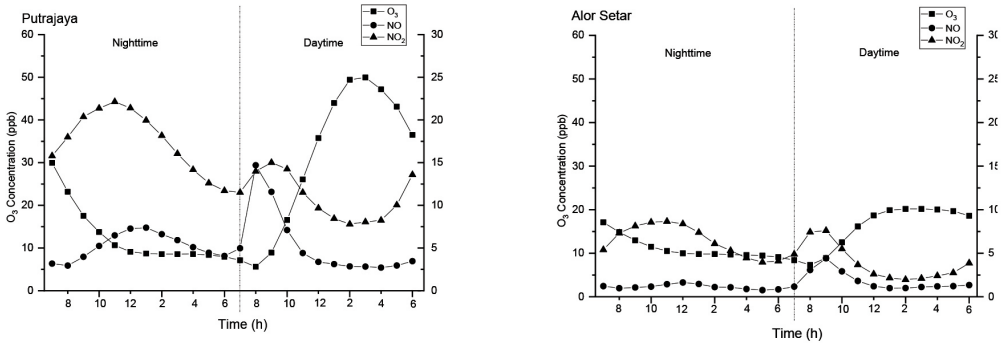

Figure 1: Diurnal variations of pollutants (O_3, NO_2, and NO) for (a) PT and (b) AS

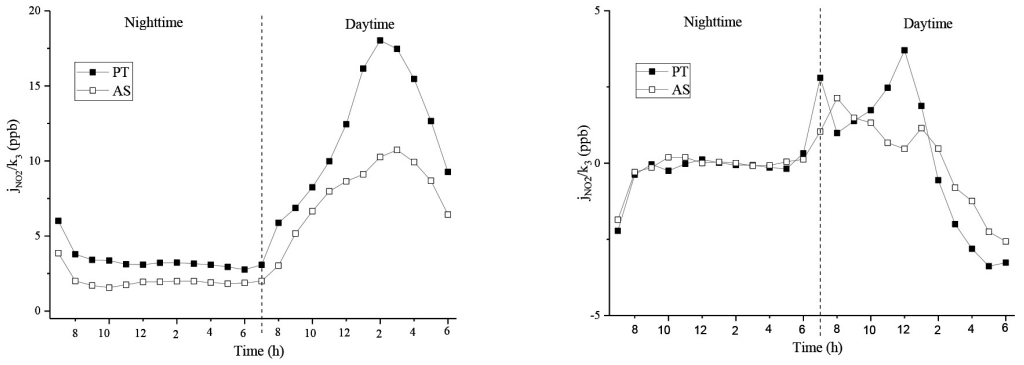

Figure 2: Diurnal variations of average (a) j_{NO_2}/k_3 and (b) $\Delta j_{NO_2}/k_3$ ratio for Putrajaya and Alor Star

Table 3: The calculated value of NO_2 photolysis rate over NO titration rate (j_{NO_2}/k_3) and their hourly differences ($\Delta j_{NO_2}/k$) for both monitoring stations

Duration	**Time**	**PT**		**AS**	
		j_{NO_2}/k_3	$\Delta j_{NO_2}/k_3$	j_{NO_2}/k_3	$\Delta j_{NO_2}/k_3$
Night-time	19:00	6.00	-2.22	3.86	-1.86
	20:00	3.79	-0.37	2.00	-0.29
	21:00	3.40	-0.04	1.70	-0.14
	22:00	3.36	-0.25	1.56	0.19*
	23:00	3.11	-0.02	1.75	0.19*
	24:00	3.09	0.12*	1.94	0.002*
	01:00	3.21	0.01*	1.94	0.03*
	02:00	3.22	-0.06	1.98	0.002*
	03:00	3.15	-0.06	1.98	-0.08
	04:00	3.09	-0.14	1.90	-0.07
	05:00	2.94	-0.18	1.82	0.04*
	06:00	2.75	0.32*	1.87	0.12*
Daytime	07:00	3.07	2.80*	1.99	1.03*
	08:00	5.88	0.98*	3.03	2.13*
	09:00	6.86	1.37*	5.16	1.48*
	10:00	8.24	1.73*	6.65	1.32*
	11:00	9.98	2.47*	7.97	0.66*
	12:00	12.45	3.70*	8.64	0.46*
	13:00	16.15	1.87*	9.11	1.14*
	14:00	18.03	-0.56	10.26	0.47*
	15:00	17.46	-2.00	10.73	-0.80
	16:00	15.46	-2.81	9.92	-1.24
	17:00	12.65	-3.38	8.68	-2.25
	18:00	9.27	-3.26	6.42	-2.56

Note: value with * are positive differences

as that obtained during daytime photochemical reactions as shown in Figure 2, the trends showing that there was titration of O_3 during night-time. O_3 concentrations during the night should be nearly zero, as there was no sunlight to enhanced O_3 formation, but this situation does not happen on both sites. Stark *et al*. (2011) stated that this could happen due to light pollution in an urban area that allows O_3 formation during the night-time from light pollution. The loss of NO has given a significant impact on night-time O_3 concentrations and next-day O_3 production because light pollution worsens the situation due to rapid urbanisation. Demands for light during night-time will continuously increase in the future as more locations are being transformed into urbanised cities, where night-time is as bright as daytime. Yusoff *et al*. (2019) found that night-time O_3 concentrations in the urban area (maximum night-time O_3 concentration 137 ppb) exceeded the limit of 100 ppb as suggested by Malaysian Air Quality Standard for ambient O_3 concentration and 27% of total monitoring stations in Malaysia having an increasing trend of night-time O_3 concentration from 2005 to 2015.

The results of the j_{NO_2}/k_3 ratio and their hourly differences are shown in Table 3. Figure 2 shows the average diurnal of the ratio NO_2 photolysis rate over NO titration rate (j_{NO_2}/k_3) and their hourly differences ($\Delta j_{NO_2}/k_3$) for both stations. j_{NO_2}/k_3 should be zero during night-time due to the absence of the photochemical reactions (Awang *et al*., 2018a; 2018b). However, results from both stations have a minimum j_{NO_2}/k_3 ratio recorded around 1.50 ppb (AS) and 2.70 ppb (PT). However, during night-time the $\Delta j_{NO_2}/k_3$ at the current hour indicates the positive differences between rates of NO_2 photolysis. During the night, the highest positive $\Delta j_{NO_2}/k_3$ lead to O_3 accumulation occurred between 22:00 to 23:00 at 0.19 ppb, which occur at AS, suggesting that formation of O_3 was the higher between both at that particular hour. This tends to be higher than what was found by Awang *et al*. (2016) in the urban site (Kota Bharu) at 0.10 ppb at 23:00. Hence, the occurrence of night-time O_3 is something that should be given due attention.

Conclusion

The variability in ground-level O_3 concentration during night-time at urban was not mainly corresponded to different precursors' concentrations, it also affected by light pollution in the cities. The variability concentration of night-time ground-level O_3 in PT was higher than AS. The titration effect of NO_2 and NO emitted from anthropogenic sources in the urban, which has the highest NO_2 and NO levels compared to other sites, may be the primary driving force of the lower value of night-time O_3. Lower rate of NO titration directly minimised the O_3 sinking process and allow ground-level O_3 to remain during night-time. During the night, titration of ground-level O_3 occurred, resulted in, instead of zero, the minimum value of ratio j_{NO_2}/k_3 recorded around 1.50 ppb (AS) and 2.70 ppb (PT), suggesting that light pollution in urban sites as the positive $\Delta j_{NO_2}/k_3$ and could lead to O_3 accumulation at night.

Acknowledgements

The authors would like to express their gratitude to Universiti Sains Malaysia and the Department of Environment, Malaysia. This study was funded under the research university individual grant (1001/PAWAM/814278).

Abbreviations: O_3: Ground-level ozone, VOCs: Volatile organic compounds, HO_x: hydrogen oxide radicals, NO: nitrogen oxides, NO_2: nitrogen dioxide, N_2O_5: dinitrogen pentoxide, NO_3: nitrate radical, PT: Putrajaya, AS: Alor Setar,

References

Alvarez, E., De Pablo, F., Tomás, C., & Rivas, L. (2000). Spatial and temporal variability of ground-level ozone in Castilla-Leon (Spain). *International Journal of Biometeorology, 44*, 44-51.

Awang, N. R., Ramli, N. A., Yahaya, A. S., & Elbayoumi, M. (2015). High nighttime ground-level ozone concentrations in Kemaman: NO and NO_2 concentrations attributions. *Aerosol and Air Quality Research*, *15*(4), 1357-1366.

Awang, N. R., Ramli, N. A., Shith, S., Yusof, N. F. F. M., Zainordin, N. S., Sansuddin, N., & Ghazali, N. A. (2018a). Time effects of high particulate events on the critical conversion point of ground-level ozone. *Atmospheric Environment*, *187*, 328-334.

Awang, N. R., Ramli, N. A., Shith, S., Zainordin, N. S., & Manogaran, H. (2018b). Transformational characteristics of ground-level ozone during high particulate events in the urban area of Malaysia. *Air Quality, Atmosphere & Health*, *11*(6), 715-727.

Banan, N., Latif, M. T., Juneng, L., & Ahamad, F. (2013). Characteristics of surface ozone concentrations at stations with different backgrounds in the Malaysian Peninsula. *Aerosol and Air Quality Research*, *13*, 1090-1106.

Clapp, L. J., & Jenkin, M. E. (2001). Analysis of the relationship between ambient levels O_3, NO_2 and NO as a function of NO_X in the UK. *Atmospheric Environment*, *35*, 6391-6405.

Duce, R. A., LaRoche, J., Altieri, K., Arrigo, K. R., Baker, A. R., Capone, D. G., Cornell, S., Dentener, F., Galloway, J., Ganeshram, R. S., & Geider, R. J. (2008). Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science*, *320*(5878), 893-897.

Ghazali, N. A., Ramli, N. A., Yahaya, A. S., Yusof, N. F. F. M., Sansuddin, N., & Al Madhoun, W. A. (2010). Transformation of nitrogen dioxide into ozone and prediction of ozone concentrations using multiple linear regression techniques. *Environment Monitoring Assessment*, *165*, 475-489.

Han, S., Bian, H., Feng, Y., Liu, A., Li, X., Zeng, F., & Zhang, X. (2011). Analysis of the relationship between O_3, NO, and NO_2 in Tianjin China. *Aerosol and Air Quality Research, 11*, 128-139.

Hassan, I. A., Basahi, J. M., Ismail, I. M., & Habeebullah, T. M. (2013). Spatial distribution and temporal variation in ambient ozone and its associated NO_x in the atmosphere of Jeddah City, Saudi Arabia. *Aerosol and Air Quality Research*, *13*, 1712-1722.

Klein, A., Ravetta, F., Thomas, J. L., Ancellet, G., Augustin, P., Wilson, R., Dieudonné, E., Fourmentin, M., Delbarre, H., & Pelon, J. (2019). Influence of vertical mixing and nighttime transport on surface ozone variability in the morning in Paris and the surrounding region. *Atmospheric Environment*, *197*, 92-102.

Kulkarni, P. S., Bortoli, D., & Silva, A. (2013). Nocturnal Surface ozone enhancement and trend over urban and suburban sites in Portugal. *Atmospheric Environment, 71*, 251- 259.

Latif, M. T., Huey, L. S., & Juneng, L. (2012). Variations of the surface ozone concentration across the Klang Valley, Malaysia. *Atmospheric Environment, 61*, 434-445.

Light Pollution Map (2018). Earth Observation Group, NOAA National Geophysical Data Center. Retrieved from https://www.lightpollutionmap.info/#zoom=4&lat=5759860&lon=1619364&layers=B0FFFFTFFFF.

Mohammed, N. I., Ramli, N. A., & Yahya, A. S. (2012). Ozone phytotoxicity evaluation and prediction of crops production in Tropical Regions. *Atmospheric Environment, 68*, 343-349.

Morris, G. A., Hersey, S., Thompson, A. M., Pawson, S., Nielsen, J. E., Colarco, P. R., McMillan, W. W., Stohl, A., Turquety, S., Warner, J., & Johnson, B. J. (2006). Alaskan and Canadian forest fires exacerbate ozone pollution over Houston, Texas, on 19 and 20 July 2004. *Journal of Geophysical Research: Atmospheres*, *111*(D24).

Seinfeld, J., & Pandis, S. (2006). Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Second Edition. New Jersey: John Wiley & Sons Inc.

Stark, H., Brown, S. S., Dube, W. P., Wagner, N., Ryerson, T. B., Pollack, I. B., Elvidge, C. D., Ziskin, D., & Parrish, D. D. (2010). Nighttime photochemistry: nitrate radical destruction by anthropogenic light sources. In *AGU Fall Meeting*.

Stark, H., Brown, S. S., Wong, K. W., Stutz, J., Elvidge, C. D., Pollack, I. B., Ryerson, T. B., Dube, W. P., Wagner, N. L., & Parrish, D. D. (2011). City lights and urban air. *Nature Geoscience*, *4*(11), 730.

Strode, S. A., Ziemke, J. R., Oman, L. D., Lamsal, L. N., Olsen, M. A., & Liu, J. (2019). Global changes in the diurnal cycle of surface ozone. *Atmospheric Environment*, *199*, 323-333.

West, J. J., Fiore, A. M., Horowitz, L. W., & Mauzerall, D. L. (2006). Global health benefits of mitigating ozone pollution with methane emission controls. *Proceedings of the National Academy of Sciences*, *103*(11), 3988-3993.

Yan, Y., Lin, J., & He, C. (2018). Ozone trend over the United States at different times of the day. *Atmospheric Chemistry and Physics*, *18*, 1185-1202.

Yusoff, M. F., Latif, M. T., Juneng, L., Khan, M. F., Ahamad, F., Chung, J. X., & Mokhtar, A. A. A. (2019). Spatio-temporal assessment of nocturnal surface ozone in Malaysia. *Atmospheric Environment*, *207*, 105-116.

Zhang, R., Lei, W., Tie, X., & Hess, P. (2004). Industrial emissions cause extreme diurnal urban ozone variability. *Proceedings of National Academic Science USA*, *101*, 6346-6350.