Assessment of Nighttime Ground Level Ozone Concentration in Klang During Wet and Dry Month

IOP Conf. Series: Earth and Environmental Science **596** (2020) 012064 doi:10.1088/1755-1315/596/1/012064

Assessment of Nighttime Ground Level Ozone Concentration in Klang During Wet and Dry Month

Amni Umirah Mohamad Nazir[1], Norrimi Rosaida Awang[1*], Siti Nurhaliza Hamidi[1], Nor Azam Ramli[2] and Nurazim Ibrahim[3]

[1] Faculty of Earth Science, Universiti Malaysia Kelantan Jeli Campus, Jeli, Malaysia
[2] School of Civil Engineering, Universiti Sains Malaysia Engineering Campus, Nibong Tebal, Malaysia
[3]Department of Civil Engineering, Faculty of Engineering, Science & Technology, Infrastructure University Kuala Lumpur,

E-mail: norrimi.a@umk.edu.my

Abstract. Ground level ozone (O_3) is the most significant secondary air pollutants in Malaysia, and this air pollutant exhibited different variations during daytime and nighttime due to differences in photochemistry. This utilizing seven variables (O_3, NO_2, NO, SO_2, PM_{10}, temperature, and relative humidity) secondary data acquired from the Air Pollution Division, Department of Environment Malaysia. The nighttime data (7 p.m. – 6 p.m.) on March and December 2015 were used to represent the dry and wet months, respectively. Box and whisker plots were used to show the variation of nighttime O_3, NO_2, NO, SO_2, PM_{10}, temperature, and relative humidity during the dry and wet months. Results suggested that there are variations among the selected variables between dry and wet month with temperature, O_3, NO_2, and PM_{10} showed higher value during dry month compared to wet month. Meanwhile, relative humidity, NO, and SO_2 showed the opposite result.

1. Introduction

Ground-level ozone (O_3) identified as the second most significant air pollutants in Malaysia and other countries worldwide. Unlike other air pollutants that have been emitted from sources, O_3 is a secondary air pollutant freshly created in the ambient air through photochemical reactions. The main ingrediants for O3 photochemical reactions are nitrogen oxide (NOx), volatile organic compounds (VOCs), and sunlight as the main reactions catalyst. Consequently, various research reported that O_3 concentrations heavily depend on the precursors concentration and the availability of sunlight to complete the photochemical reactions [1, 2].

Ground-level ozone exhibited complete different diurnal variations compared to other primary air pollutants such as NOx which normally reached peak concentration coincided with morning and evening rush hour as the vehicle emission are their main source. Meanwhile, O_3 showed a clear trend that is very close to sunlight diurnal trends where peaks concentration normally recorded in the afternoon or early evening [2, 3]. Normally O_3 concentration is low in the morning as the minimum concentration usually recorded at 8.00 a.m due to a high rate of nitric oxide (NO) titration reactions [4, 5], and the decreasing trend was also reported during the evening [3, 6].

Comparatively, O_3 concentrations are higher during daytime than nighttime due to the availability of photochemical reactions only during daytime [6, 7]. In the absence of photochemical reactions that responsible for supplying fresh O_3, the level of O_3 concentrations are maintained at a low concentration around ten ppb [8] Further reduction of nighttime O_3 concentration were promoted by other nighttime chemical removals such NO titration as well as deposition and transportation processes [1]. Considering the significant different in chemical reactions between daytime and nighttime, several studies separating the daytime and nighttime analysis to increase the accuracy of results [1, 9]

Ground-level ozone research normally more focusing on daytime O_3 concentration due to a higher risk of the pollutant towards human health, crop yield, and the environment [10, 11]. However, the variations of nighttime O_3 concentrations received substantial scholarly attention among researchers. Awang and Ramli [3], elucidated that nighttime depletion in O_3 concentrations would influence the next day's O_3 concentrations. Previously, Awang et al. [1] reported there are ocassions of high nighttime O_3 concentrations were recorded in Kemaman attributed by restricted nighttime sinking agents in the area, thus, reducing the depletion rates and allowed O_3 to remain in the atmosphere. Mavrakis et al. [12] also reported there was a case of high nighttime O_3 concentration over the Greater Athens area were recorded. However, the study claimed that a high nighttime O_3 concentration case was resulted by free troposphere-atmospheric boundary layer interaction allowing transportation of stratospheric O_3 to earth surface that will consequently increasing ground-level ozone. Even the claimed was supported by mesoscale modeling and hydraulic theory, but the occasion of such an event was unpredictable and not well understood.

Ghosh et al. [13] claimed that nighttime O_3 variations largely controlled by the NO_2-NO_3-N_2O_5 cycle as the cycle responsible for the O_3 depletion process. The reported result was also in line with Goliff et al. [14] that claimed NO_3 radical plays an important role in regulating nighttime air quality under desert conditions. According to Ghosh et al. [13] and Godiff et al. [14], the end product of the cycle reactions is the production of nitric acid (HNO_3) before O_3 was removed from the atmosphere in the form of precipitation. Considering the situation, ambient air humidity might also be the controlling factor that further enhances O_3 nighttime chemistry. However, such a relationship not been explored, limiting the understanding the nighttime O_3 chemistry. So, this study aims to determine the effect of air humidity toward the nightime ozone removal by focusing on wet and dry months in Malaysia. The inluenced of relative humidity towards the nighttime O_3 removal would beneficial in O3 control policies and strategies.

2. Material and Methods

2.1 Sites Description

This study selected Klang [N03˚00.620'; E101˚24.484] continuous air monitoring station as a study area. Klang covered around 636 km^2 which also known as a port city. Klang located in Selangor State, which is an urban area with various industrial activities and congested roads during morning and evening peak hours. In the 2010 census, the total number of population that resided in Klang area is around 832,600, and the number is expected to grow in 2020. Climatically, Klang also experiences a tropical rainforest climate distinguished by high temperature and relative humidity with heavy seasonal rains during the northeast monsoon (November to January) [15].

2.2 Measurement and instrumentation

Continuous hourly O_3, NO_2, NO, SO_2 and PM_{10} concentrations together with temperature and relative humidity data for two months March and December 2015 were obtained from the Air Quality Division of the Department of Environment, Ministry of Natural Resources and Environment of Malaysia. The obtained secondary data are regularly subjected to standard quality control processes and quality assurance procedures [16]. The procedures used for continuous monitoring are in accordance with the standard procedures outlined by internationally recognized environmental agencies such as the United States Environmental Protection Agency [17].

Hourly O_3 concentration was monitored using the Model 400E UV Absorption Ozone Analyzer [18]. The analyzer was utilizing the Beer-Lambert Law, which based on the internal electronic resonance of O_3 molecules with the absorption of 254 nm UV light in measuring low ranges of O_3 concentration in ambient air [7, 16]. Ambient NO_2 and NO concentrations were collected using the Model 200A NO/NO_2/NOx Analyzer [7, 17]. This analyzer applies chemiluminescence detection principles to detect NO_2 concentrations in ambient air and has been proven to

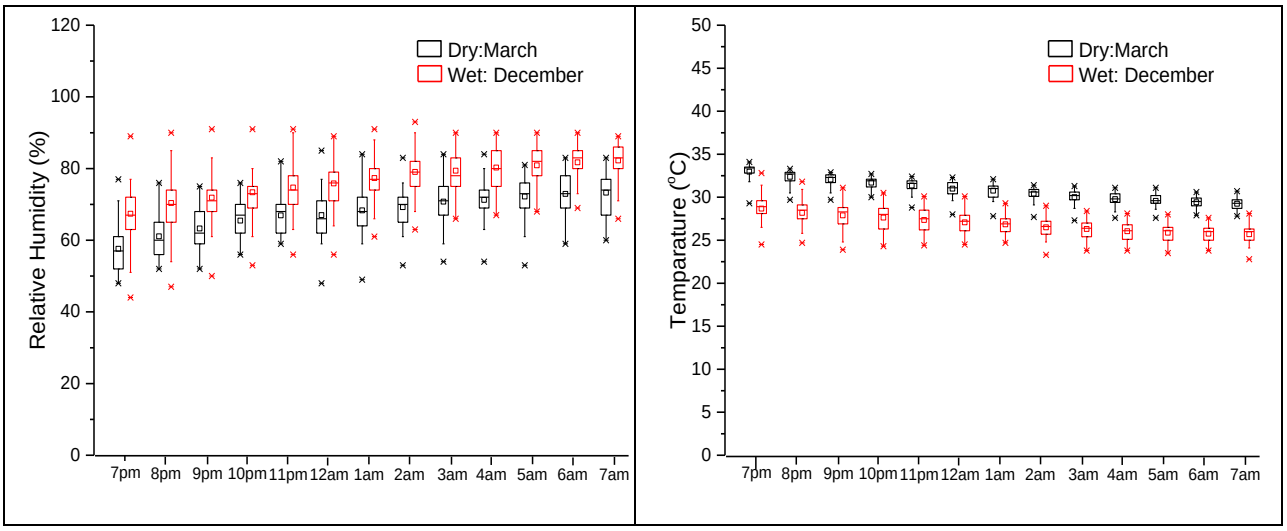
produce sensible, stability, and ease of use for ambient or dilution continuous monitoring [18]. Hourly average temperature and relative humidity were measured with MET One 062 sensor and MET One 083D sensor, respectively.

Based on local time, nighttime hours are lies between 7 p.m. to 7 a.m. [16]. Ozone measured between 7 a.m. to 7 p.m. is considered as daytime ozone, while ozone measured between 7 p.m. to 7 a.m. is deemed as nighttime ozone. Meanwhile, March was considered as the dry month, while December was considered as a wet month coincided with the monsoon season.

3. Result and Discussion

3.1 Box and whisker plot during the dry and wet month

Box and whisker plot that illustrated variations of relative humidity, temperature O_3, NO_2, NO, SO_2, and PM_{10} concentrations during the dry month (March) and wet month (December) in 2016 were shown in Figure 1(a) to Figure 1(g), respectively. Results clearly showed that there are significant differences for all parameters during the dry and wet months due to differences in atmospheric conditions. Figure 1(a) showed that relative humidity during the wet month was significantly higher than during dry month with the are value in the range of 70-80% (wet) and 60-70% (dry). However, both dry and wet month show similar diurnal trend as the relative humidity gradually increase throughout nighttime. High relative humidity normally associated with a rain event, while dry ambient air would subsequently be lowering the relative humidity. The variation in hourly temperature (Figure 1(b)) showed the opposite trend to relative humidity. The higher temperature was recorded in the dry month as compared to wet month with average nighttime temperature was consistently below 30˚C.



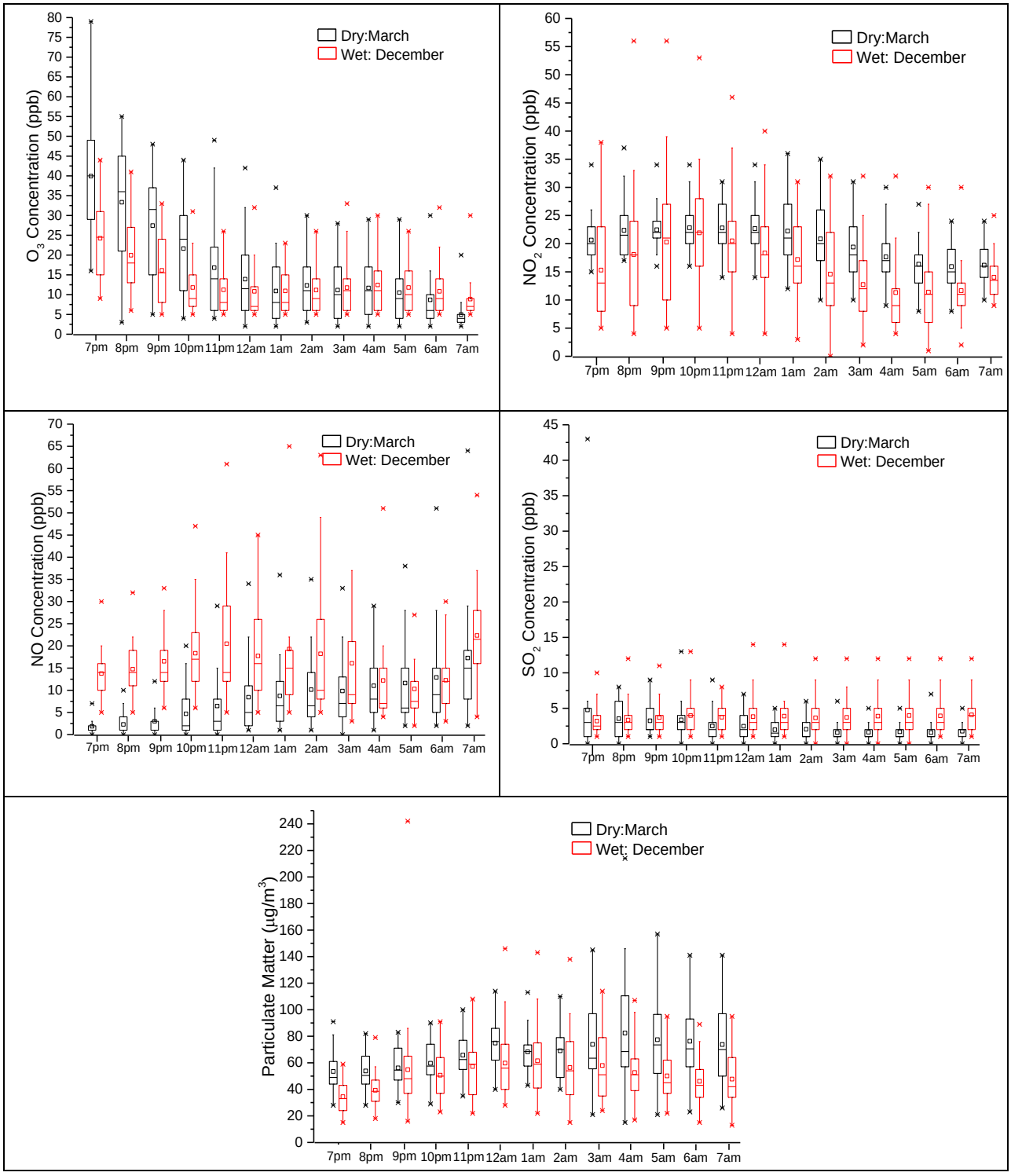


Figure 1. Box and whisker plot of (a) relative humidity during; (b) temperature; (c) O_3 concentration; (d) NO_2 concentration; (e) NO concentration; (f) SO_2 concentration; (g) PM_{10} concentration during the dry and wet month

Figuratively, O_3 concentration during the dry month was significantly higher than in the wet month. However, the statement only true from 7 p.m. until 2 a.m. as the result showed the opposite trend as the nighttime O_3

concentration in wet month surpassing the dry month concentration at 3 a.m. until 7 a.m. Nighttime O_3 concentrations normally being destructed by chemical reactions as well as deposition and transportation process. Nevertheless, low nighttime O_3 concentration is mainly attributed by ceasing in photochemical reactions due to the absence of sunlight. The result suggested that, after the cease of photochemical reactions at approximately 7 p.m., O_3 concentrations were around 40 ppb (dry) and 25 ppb (wet), and the nighttime O_3 concentration continued to decrease in the early morning. The plot suggested that O_3 concentration for both months showed higher variance based on larger differences between Q3 and Q1 (box) in early nighttime (7 p.m. – 12 a.m.) before beginning to be constant afterward.

In contrast to O_3 and NO_2 concentrations variation, nighttime NO concentrations during the wet month were higher than during dry month. According to Banan et al. [19], daily vehicle emission plays the most important rule in regulated NO concentrations variations becausemost of the NO concentrations in ambient air produced by vehicle emissions.

Reported by many studies [6, 9, 20] nighttime ozone chemistry showed completely opposite chemistry with daytime ozone with the predominantly reactions stated in reaction (R1) – (R4). According to Awang et al. [3], nighttime O_3 chemistry is predominantly controlled by the reaction by NO and O_3 concentrations, which NO titration process/reaction (R1). High NO concentration produced by vehicular and industrial emission would promote (R1), thus destroying O_3 in the air. In addition, the reaction between O_3 and NO_2 during nighttime (R2) also capable of destroying nighttime O_3 concentration by converting into nitrate (NO_3), which later reacts with NO_2 to form dinitrogen pentoxide (N_2O_5) (R1). The N_2O_5 concentration will then react with water in ambient air to form nitric acid and remove from ambient air in form acid rain or acid precipitation. The effect of (R1) – (R4) clearly illustrated in Figure 1 (c) as nighttime O_3 is significantly lower during the wet month due to high moisture content in ambient air that promotes R4 in addition to the wet deposition that would also been enhanced during the wet month.

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R1)}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R2)}$$

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \quad \text{(R3)}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad \text{(R4)}$$

Figure 1(f) shows box and whisker plots of SO_2 in Klang during the dry and wet months. Results suggested that the SO_2 concentrations in both dry and wet months not surpassing five ppb, which considered a very low in concentration. The SO_2 concentration was significantly higher during the wet month compared to dry month with only around 2 - 3 ppb different in average concentrations. The result is in line with Zhang et al. [21] finding that reported SO_2 concentration increase with increasing air humidity. Additionally, according to Salahudin et al. [22], the major sources of SO_2 in Malaysia is power generation industries followed by processing industries and motor vehicle emission.

Even though SO_2 is also a significant primary air pollutant, it is not an O_3 precursor. Wilson et al. [23] in his study about the role of SO_2 in photochemical smog elucidated that SO_2 does not directly react with either O_3 and NO_2 in ambient air. Still, the reactions can occur in solution or surfaces. The study added the only reactions SO_2 react with either O_3 and NO_2 are through NO_3 and N_2O_5 and only occurred during nighttime. When O_3 and NO_2 react in (R2), the reactions produce NO_3. The produce NO_3 could react back with NO_2 (R3) to produce N_2O_5 or react with SO_2 (R5) to reproduce NO_2. Meanwhile, N_2O_5 could also react with SO_2 (R6), producing sulfur trioxide (SO_3) with later can react with water and producing sulphuric acid (H_2SO_4) (R7). Reactions (R5), (R6) and (R7) is another path of nighttime O_3 removal as well as NO_2 and SO_2 removal. These reactions might also contribute low nightime O3 concentration in the wet month since nighttime SO_2 concentration is significantly higher than in a dry month, thus promoting a higher rate of (R5), (R6) and (R7).

$$NO_3 + SO_2 \rightarrow SO_3 + NO_2 \quad \text{(R5)}$$

$$N_2O_5 + SO_2 \rightarrow SO_3 + 2NO_2 \quad \text{(R6)}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad \text{(R7)}$$

Figure 1(g) shows nighttimePM_{10} concentration in Klang during the dry and wet months. Result clearly suggest that nighttime PM_{10} concentrations significantly lower during the wet month than in a dry month. Various studies have demonstrated that wind speed and relative humidity are the two most important external meteorological factors affecting the mass concentration of aerosols. Fundamentally, PM_{10} and relative humidity is inversely related because generally PM_{10} pollution was worse in the low relative humidity and better in higher relative humidity. According to Li et al. [30], during high humidity, particulates absorb more water resulting increment in size and volume and subside to the ground with the gravity. Moreover, high relative humidity may also indicate more precipitations events promoting higher wet deposition and lowering PM_{10} concentrations.

Conclusion

The main motivation of this study is to explore on the nighttime O_3 chemistry, especially the effect of relative humidity by comparing variations of nighttime O_3 concentrations during the dry and wet month. Results clearly showed that there is significant difference for all parameters during the dry and wet month. The differences in atmospheric conditions based on the recorded relative humidity in the range of 70-80% (wet) and 60-70% (dry) with higher temperature recorded during the dry month. Nighttime O_3 concentration is significantly higher during the dry month compared to wet based on average concentration of 40 ppb (dry) and 25 ppb (wet). A similar result also has been exhibited by NO_2 and PM10 as the dry month concentrations are higher than the wet month. However, the opposite relationship was observed for NO and SO_2 as these pollutants in Klang showed higher concentrations.

Acknowledgments

The authors are grateful to the Ministry of Higher Education under Fundamental Research Grant Scheme (FRGS) (R/FRGS/A0800/01525A/003/00554) for funding this study and to the Department of Environment for providing data in the selected location. The authors also thank Universiti Malaysia Kelantan for providing the best facilities for this study.

References

[1] Awang, N.R., Ramli, N.A., Yahaya, A.S. and Elbayoumi, M. (2015). High Nighttime Ground-Level Ozone Concentrations in Kemaman: NO and NO_2 Concentrations Attributions *Aerosol and Air Quality Research,* **15**, 1357-1366.

[2] Mohamed-Noor, N., Mohamad-Hasim, N.I. and Yusof, S.Y. (2018). Variation of Ground-Level Ozone Concentration in Urbanized Area in Malaysia. *IOP conference Series: Materials Science and Engineering,* **374**, 1-6.

[3] Awang, N. R., and Ramli, N.A. (2017). Preliminary Study of Ground Level Ozone Nighttime Removal Process in an Urban Area. *Journal Tropical Resources Sustainable Science,* **5**, 83-88.

[4] Abd-Rani, N. L., Azid, A., Khalit, S.I., Juahir, H., and Samsudin, M.S. (2018). Air Pollution Index Trend Analysis in Malaysia, 2010-15 *Polish Journal of Environmental Studies,* **27**(2), 801-807.

[5] Mohamad-Hashim, N.I. and Mohamed-Noor, N. (2017). Variations of Ground-level Ozone Concentration in Malaysia: A Case Study in West Coast of Peninsular Malaysia. *MATEC Web of Conferences,* **97**, 1-6.

[6] Awang, N.R., Ramli, N.A., Yahaya, A.S., and Elbayoumi, M. (2015). Multivariate methods to predict ground level ozone during daytime, nighttime, and critical conversion time in urbans areas. *Atmospheric Pollution Research,* **6**, 726-734.

[7] Ghazali, N.A., Ramli, N.A., Yahaya, A.S., MD-Yusof, N.F.F., Sansuddin, N. and Al-Madhoun, W.A. (2010). Tranformation of nitrogen dioxide into ozone and prediction of ozone concentrations using multiple linear regression techniques. *Environmental Monitoring and Assessment,* **165**(1-4), 475-489.

[8] Mohamed-Noor, N., Mohamad, N.N., and Mohamad-Hashim, N.I. (2018). Variation of Ground-level Ozone in the West Coast of Peninsular Malaysia. *EnvironmentAsia,* **11**(3), 235-250.

[9] Warmiński, K. and Bes, A. (2018). Atmospheric Factors Affecting a Decrease in the Night-Time Concentrations of Tropospheric Ozone in a Low-Polluted Urban Area. *Water Air Soil Pollut,* **229**(350), 1-13.

[10] Garthwaite R.,F.D., Stevenson D., P., Ashmore M., Grennfelt P., Amann M., Anderson R., Depledge M., Derwent D., Hewitt N., Hov O., enkin M., Kelly F., Liss P., Pilling M., Pyle J., and Slingo J. (2009). Ground level ozone in the 21st century: Trends, interactions with climate and environmental impacts. *IOP Conference Series: Earth and Environmental Science,* **6**, 1-3.
[11] Gautam, P., Srivastava R.K., and Dr. G. Beig. (2016). Ozone Variation at Jabalpur and Inter Relationship Study with Various Meteorological Parameters *Global Journal of Science Frontier Research (H),* **16**(1), 15-24.
[12] Mavrakis, A., Flocas, H. A., Mavromatidis, E., Kallos, G., Theharatos, G., and Christides, A. (2010). A case of nighttime high ozone concentration over the greater Athens area. *Meteorologische Zeitschrift,* **19**(1), 035-045.
[13] Ghosh, D., Lal, S. and Sarkar, U. (2013). High Nocturnal Ozone Levels at a Surface Site in Kolkata, India: Trade-off between Meteorology and Specific Nocturnal Chemistry. *Urban Clim,* **5**, 82-103.
[14] Goliff, W. S., Luria, M., Blake, D.R., Zielinska, B., Hallar, G., Valente, R.J., Lawson, C.V., Stockwell, W.R. (2015). Nighttime air quality under desert conditions. *Atmospheric Environment,* **114**, 103-111.
[15] Sulong, I., Mohd-Lokman, H., Mohd-Tarmizi, K., and Ismail, A.,. (2002). Mangrove Mapping using Landsat Imagery and Aerial Photographs: Kemaman District, Terengganu, Malaysia. *Environment, Developement and Sustainability,* **4**, 135-152.
[16] Mohamed, N.I., Ramli, N.A. and Yahya, A.S. (2013). Ozone Phytotoxicity Evaluation and Prediction of Crops Production in Tropical Regions. *Atmospheric Environment,* **68**, 343-349.
[17] Latif, M. T., Dominick, D., Ahamad, F., Khan, M.F., Juneng, L., Hamzah, F.M., and Nadzir, M.S.M. (2014). Long Term Assessment of Air Quality from a Background Station on the Malaysian Peninsula. *Science of the Total Environment,* **482,** 336-348.
[18] DoE. (2015). Air Quality. Department of Environment, Ministry of Sciences, Technology and the Environment, Malaysia, Kuala Lumpur
[19] Banan N., L. M. T., Juneng L., and Ahamad F. (2013). Characteristics of Surface Ozone Characteristics at Stations with Different Backgrounds in the Malaysian Peninsula. *Aerosol and Air Quality Research,* **13**, 1090-1106.
[20] Brown, S. S., and Stutz, J.,. (2012). Nighttime radical observations and chemistry. *The Royal Society of Chemistry,* **41**, 6405-6447.
[21] Zhang, M., Ma, Y., Gong, W., Wang, L., Xia, X., Che, H., Hu, B., and Liu, B. . (2017). Aerosol radiative effect in UV, VIS, NIR, and SW spectra under haze and highhumidity urban conditions. *Atmospheric Environment,* **166**, 9-21.
[22] Salahudin, S. N., Abdullah, M.M. and Ahmad-Newaz, N. (2013). Emissions: Sources, Policies and Development in Malaysia. *International Journal of Education and Research,* **1**(7), 1-12.
[23] Wilson Jr., W. E., Levy, A. & Wimmer, D.B. . (1972). A Study of Sulfur Dioxide in Photochemical Smog. Journal of the Air Pollution Control Association, **22**(1), 27-32.
[24] Li, X., Ma, Y., Wang, Y., Liu, N. and Hong, Y. (2017). Temporal and spatial analyses of particulate matter (PM_{10} and $PM_{2.5}$) and its relationship with meteorological parameters over an urban city in northeast China. *Atmospheric Research,* **198**, 185–193.