



Transformational characteristics of ground-level ozone during high particulate events in urban area of Malaysia

Norrimi Rosaida Awang¹ · Nor Azam Ramli² · Syabiha Shith² · Nazatul Syadia Zainordin² · Hemamalini Manogaran¹

Received: 24 October 2017 / Accepted: 18 April 2018
© Springer Science+Business Media B.V., part of Springer Nature 2018

Abstract

Observations of ground-level ozone (O₃), nitric oxide (NO), nitrogen dioxide (NO₂), particulate matter (PM₁₀) and meteorological parameter (temperature, relative humidity and wind speed) fluctuations during high particulate event (HPE) and non-HPE in Malaysia have been conducted for 2 years (2013 and 2014). The study focuses on urban areas, namely, Shah Alam, Petaling Jaya and Bandaraya Melaka. The diurnal variations of ground-level O₃ concentration were higher during HPE than those during non-HPE in all urban areas. The concentration of O₃ fluctuated more in 2014 than 2013 due to the higher incidences of HPE. Temperature and wind speed fluctuated with higher PM₁₀, NO₂ and NO concentrations during HPE than those during non-HPE in all urban sites. Relative humidity was lower during HPE than that during non-HPE. Positive correlations were found between PM₁₀ and ozone during HPE for Shah Alam and Petaling Jaya with 0.81 and 0.79, respectively. Meanwhile, negative correlation (−0.76) was recorded for Bandaraya Melaka. The non-HPE correlation of PM₁₀ and O₃ showed negative values for all locations except Petaling Jaya (0.02). Temperature and wind speed shows a strong positive correlation with ozone for all locations during HPE and non-HPE with the highest at Shah Alam (0.97). Inverse relationships were found between relative humidity and O₃, in which the highest was for Shah Alam (−0.96) in 2013 and Shah Alam (−0.97) and Bandaraya Melaka (−0.97) in 2014. The result of the ozone best-fit equation obtained an R² of 0.6730. The study parameters had a significant positive relationship with the ozone predictions during HPE.

Keywords Ozone production · Photochemistry rate · Anthropogenic sources · Ozone precursor

Introduction

Air pollution is a worldwide issue that needs to be seriously addressed by the human society. In Malaysia, the haze phenomenon in 1997 affected the health of individuals (approximately 50% were schoolchildren) in areas as far Klang and Kuala Lumpur (Afroz et al. 2003). Urbanization is generally regarded a core development process in which the transformation of an area's natural landscape for various economic uses subsequently affects air quality (Abdullah et al. 2012), and the

increased intervention of humans with the natural environment has often resulted in the production of atmospheric pollutants. These phenomena can be explained by the increased need for transportation, energy production and consumption and industrial processes, all of which contribute to unhealthy air quality (Rai et al. 2011). Among the various pollutants found in the atmosphere, the ground-level ozone (O₃) remains to be one of the most critical air pollutants because of its proven impact towards human health, cropland and natural areas (Abdul-Wahab et al. 2005).

Ozone, a major component of photochemical smog, is a key precursor of hydroxyl radical (OH) that controls the oxidizing power of the atmosphere (Abdul-Wahab et al. 2005; Toro and Seguel 2015). Ozone in the lower part of the atmosphere (troposphere) is regarded the most widespread source of global air pollution. Chooi et al. (2014) reported that ozone in the earth atmosphere is the major absorber of infrared radiation and contributes approximately 3–7% of greenhouse gas. Awang et al. (2015) reported that ground-level ozone (O₃) is a secondary air pollutant resulting from high anthropogenic

✉ Nor Azam Ramli
ceazam@usm.my

¹ Faculty of Earth Science, Universiti Malaysia Kelantan Kampus Jeli, Locked Bag No. 100, 17600 Jeli, Kelantan, Malaysia

² Environmental Assessment and Clean Air Research, School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

activities. Ground-level ozone is classified as a secondary air pollutant (Chooi et al. 2014; Awang et al. 2000) that contributes to the atmospheric heating of the troposphere; incidentally, it is not included in the list of emission inventories (Abdul-Wahab et al. 2005).

The inevitable rise of the global population will drive processes that will likely lead to the initialization of ozone precursors. This phenomenon accords with the findings of Sicard et al. (2009) and Zhao et al. (2015) which report that the increase in industrial activities, motorized traffic and agricultural activities will lead to the incremental increase of several air pollutants, such as sulphur dioxide (SO₂), nitric oxides (NO), volatile organic compounds (VOCs), carbon monoxide (CO) and methane (CH₄) (Toro et al. 2014). Meteorology is another influential factor of the future trend of ozone concentrations. Apart from emissions, the formation, destruction and transport of ozone will greatly depend on meteorological factors, such as temperature, humidity and rainfall (Sicard et al. 2009).

A high particulate event is defined as the condition wherein the readings of an environmental application program interface (API) consecutively exceeds 100 for a 72-h period or longer. The coefficient of haze (COH), an API measure, represents the level of visibility interferences in the atmosphere (McNaught and Wilkinson 1997). A haze phenomenon differs from fog or mist which consists of 90% water. By contrast, the basic components of haze particles comprise chemical substances, such as ozone, sulphur dioxide, nitric oxide, VOCs, carbon monoxide, carbon dioxide, metals, nitric acid, nitrates, sulphuric acid and sulphates (Liu et al. 2016).

East Asia is regarded the largest global source of aerosols and trace gases. However, the state of Asian dust and haze particles in the troposphere usually depend on the physical (particle size, number and spatial distribution) and chemical properties (particle composition, mixing state and hygroscopicity) of local aerosols (Li et al. 2014). The presence of aerosols in the upper atmosphere, which are strongly related with global and regional climatic conditions, are likely to absorb solar radiation (Tomasi et al. 2007) and modify the sun's radiative properties (Reid et al. 1998; Bo et al. 2010; Li et al. 2010; Zhang et al. 2017). This condition can be referred as direct short-wave aerosol radiative forcing (ARF) which differs from the net short-wave radiation fluxes with and without the presence of aerosols in cloud-free conditions (Bi et al. 2014). A study conducted on January 2013 found that the mean absorption of sunlight by aerosols in Beijing was extremely strong and the haze particles strongly scattered the sunlight in the area (Bi et al. 2014).

The absorption and scattering of sunlight may have been caused by the brownish appearance of air-haze mixture (Huang et al. 2008; Ramanathan et al. 2001). A similar finding

was found by Ramanathan et al. (2001) though the Indian Ocean Experiment in which the absorbing haze decreased nearly 50% of the surface solar radiation in relation to total ocean heat flux (Huang et al. 2008). The findings emphasize the nearly doubled solar heating at the lower tropospheric part of the earth. However, measuring global aerosol properties is difficult due to the lack of important parameters needed to investigate the spatial and temporal variations of aerosols (IPCC 2007).

The light scattering effect strongly influences the amount of sunlight that penetrates the earth and the formation of ground-level ozone. In particular, sunlight acts as the major catalyst for transforming precursor atmospheric gases into ozone (Seinfeld and Pandis 2006). Given that ozone is a secondary atmospheric pollutant and requires precursors for their formation, the frequent occurrence of haze indicated by elevated API levels essentially represents the rate of transformation of ozone in the atmosphere.

In the early 1990s, an ozone prediction model by using a time series was developed to forecast daily maximum ozone levels. However, according to Yi and Prybutok (1996), the time series model utilizes past ozone levels for prediction and thus is unlikely to be effective. Subsequently, traditional stepwise regression models are used to predict the maximum ozone level (Yi and Prybutok 1996). Moreover, stepwise regression has the advantage of identifying significant independent variables with only a few steps. Such models were also utilized in the studies by Camalier et al. (2007) in which the generalized linear model with R software is used to study the relationship of urban ozone with meteorological parameters. Their study result showed that the model performed well with the value of R^2 as high as 0.80 when testing the nonlinear effects of meteorological variables. Previous studies by Wolff and Liroy (1978) focused on development of the best-fit ozone equation and showed that the regression model can be used as a simple tool to predict the maximum ozone concentrations.

Studies regarding the behaviour of ozone during high particulate events (HPE) had been conducted in Malaysia—mainly because haze is common around the country—but the work is scarce. Surged in O₃ concentrations together with other pollutants such as PM and nitrogen oxides (NO_x) during HPE would create a mixture in ambient environments and Liu and Peng (2018) reported that O₃-NO₂-PM_{2.5} mixtures may be more harmful to human health. In addition, most urban areas and tropical countries (e.g. Malaysia) have favourable meteorological conditions for conducting such studies. In Malaysia, high frequency of large scale biomass burnings is also a common scenario.

This study aims to investigate the fluctuational characteristics of ozone in urban areas and the transformational

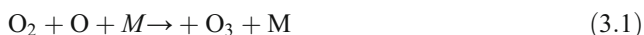
characteristics of ground-level ozone from its main precursors during HPE. An ozone best-fit model to predict next-hour ozone (i.e. $O_3(t+1)$) is also developed.

Material and method

The study area comprises three main urban areas from selected sites in Malaysia with HPE occurrence (Fig. 1). The details of the HPE occurrence with PM_{10} average for the selected sites are presented in Table 1. Secondary data are obtained from the Department of Environment of Malaysia. The pollutants considered in this study include PM_{10} and O_3 . The details of the sample collection for the secondary data are shown in Table 2. The main meteorological parameters are wind speed (WS), temperature (T) and relative humidity (RH).

Ozone photochemistry rate

The steady state of O_3 concentration is directly proportional to $(NO_2)/(NO)$ ratio. However, instead of utilizing $(NO_2)/(NO)$, this study calculated the rate of NO_2 photolysis (J_{NO_2}) as the coefficient for the reaction of NO with O_3 (k_3) (J_{NO_2}/k_3) to determine the variations in O_3 production rates during HPE and non-HPE occurrences (Clapp and Jenkin 2001, Han et al. 2011). The photostationary state of the relations of O_3 , NO and NO_2 were dominated by the reactions derived with Eqs. (3.1) to (3.3) (Jenkin and Clemitshaw 2000).



The value of J_{NO_2}/k_3 is calculated with Eq. (3.4). The differences in J_{NO_2}/k_3 value at the current hour (h_i) and the previous hour (h_{i-1}) is denoted by ($\Delta J_{NO_2}/k_3$). If the differences of the photolysis rates with the previous hour variable are positive, then NO_2 photolysis rates are higher than NO titration rates (i.e. O_3 production). By contrast, a negative difference indicates that NO_2 photolysis is lower than NO titration (i.e. O_3 destruction).

$$\frac{J_{NO_2}}{k_3} = \frac{[O_3][NO]}{[NO_2]} \quad (3.4)$$

Results and discussions

The monthly occurrences of HPE events in Malaysia from 2013 to 2014 were compared (Table 3). The HPE occurrences were the highest in Klang (maximum recorded API 358) in

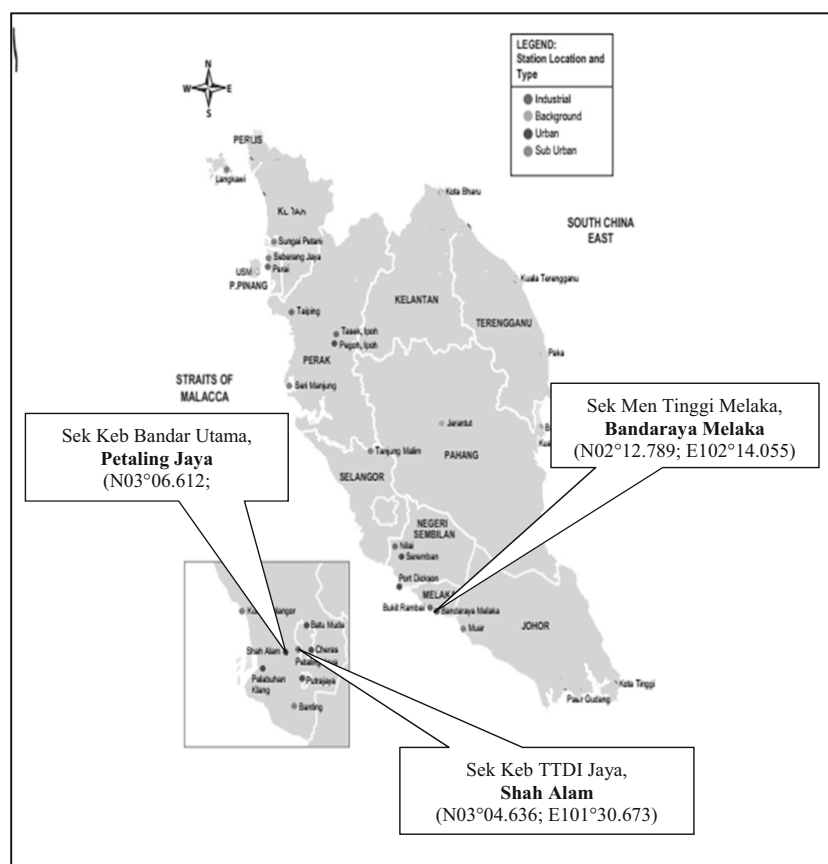
2014 and Port Dickson (maximum recorded API 335) in 2013. In Klang, HPE occurred 46 times in 2014, and the highest impact was on July in which 17 locations were affected. In Port Dickson, HPE occurred 30 times in 2013, and the highest impact was on June in which 26 locations were affected. HPE in Malaysia mainly occurs due to the relatively higher anthropogenic sources, such as biomass burning and agricultural land clearing (Norela et al. 2013). The high occurrence of HPE is also influenced by meteorological parameters, such as temperature, relative humidity, rainfall and wind direction (Amil et al. 2016; Khan et al. 2016). The diurnal plots in Fig. 2 present the detailed description of the criteria pollutants (PM_{10} , O_3 , NO_2 and NO) and meteorological parameters (T , RH and WS) during HPE and non-HPE in the selected urban sites.

Diurnal variation of O_3 , NO_2 and PM_{10} during HPE and non-HPE

O_3 exhibits strong diurnal variations that are controlled by various processes, including photochemistry and physical/chemical removal, and by deposition and transport rates (Ghazali et al. 2010; Alghamdi et al. 2014; Kumar et al. 2015). "Diurnal" means a daily cycle completed every 24 h. The elevated levels of precursor emissions from various anthropogenic activities, such as transportation (vehicular emission) and industrialization, can increase O_3 concentrations in ambient air. Apart from precursor emissions, complex meteorological conditions contribute to large diurnal differences and seasonal and yearly variations. Considering the high concentrations of particles during HPE, the photochemistry reactions may be disturbed and cause different variations in diurnal trends. Researchers mainly rely solely on API values in such conditions, but HPE cannot be described by PM_{10} diurnal variations for urban areas.

The diurnal variations of different ozone concentrations are shown in Fig. 2, in which the particulates are higher and have clearer fluctuations during HPE compared with the normal patterns during non-HPE. The fluctuations in PM_{10} concentrations can be explained by the increase in biomass burnings and forest fires, the main factors of HPE in Malaysia, and the exceedingly high number of vehicles and industrial emissions in urban areas. The O_3 concentrations exhibit similar trends as those found by Tong et al. (2017) in Ninbo, China and Gong et al. (2017), in which O_3 concentrations were lower in the early morning (7–8 a.m.) and peaked at 12 noon to 4 p.m. In general, the O_3 diurnal variation between day and night times can be distinguished by solar radiation (Awang et al. 2015; Awang et al. 2016). High O_3 concentrations coincide with the amount of high solar radiation intensity during the day, a favourable condition for initializing photochemical reactions. Tong et al. (2017) found the significant differences in O_3 concentrations level during daytime and night-time were happen

Fig. 1 Location of urban area involved in study



at different wind speeds and wind direction. In the photochemical reaction of O_3 formations, solar radiation with a wavelength of less than 400 nm has enough energy to photolyse NO_2 into NO and atom oxygen (O) (Seinfeld and Pandis 2006; Ghazali et al. 2010). During non-HPE or normal

ambient conditions, the minimum O_3 concentrations appear during night-time and early morning hours (near sunrise), with the lowest concentrations consistently measured at 8 a.m., and this scenario is mainly triggered by NO titrations. Then, by the time of the morning rush hour (6–9 a.m.), high concentrations

Table 1 Details on HPE occurrence in urban area for 2013 and 2014

Month	Stations	Period				HPE Hour	API	
		Start	Time	End	Time		Average	Maximum
2013								
June	Shah Alam	23/6	7.00 a.m.	26/6	11.00 a.m.	84	195	301
	Petaling Jaya	23/6	7.00 a.m.	26/6	11.00 a.m.	84	178	231
	Bandaraya Melaka	15/6	11.00 a.m.	17/6	11.00 a.m.	56	120	161
July	Bandaraya Melaka	19/6	7.00 a.m.	26/6	1.00 a.m.	172	156	415
		21/7	7.00 a.m.	24/7	2.00 a.m.	68	113	135
2014								
Mac	Shah Alam	8/3	10.00 a.m.	10/3	4.00 a.m.	31	118	127
		13/3	8.00 a.m.	15/3	1.00 p.m.	54	146	166
	Petaling Jaya	3/3	6.00 p.m.	4/3	5.00 p.m.	24	115	127
		8/3	10.00 a.m.	10/3	1.00 a.m.	28	116	124
		13/3	7.00 a.m.	15/3	1.00 p.m.	54	156	186
July	Bandaraya Melaka	13/3	2.00 p.m.	14/3	10.00 p.m.	33	116	128
July	Shah Alam	27/7	6.00 p.m.	29/7	3.00 a.m.	34	102	107

Table 2 Summary of data collection information in study

Type of data	Secondary Data
Instrument	UV absorption O ₃ analyzer model 400A NO/NO ₂ /NO _x analyzer model 200A
Monitoring period	12.00 a.m.–12.00 a.m
Total duration	24 h

of NO from vehicles and industrial activities are released (Jiménez-Hornero et al. 2010; Reddy et al. 2011), which accelerate the release of NO titrations in ambient atmosphere. The increase in NO titration eventually promotes the reduction of O₃ concentrations. In particular, NO titration is the most significant sink reaction of ground-level O₃ (Ghazali et al. 2010; Latif et al. 2012; Banan 2013; Alghamdi et al. 2014).

The peak concentrations during HPE in 2013 and 2014 in Shah Alam were 94.0 and 94.25 ppb, and the corresponding non-HPE concentrations were 48 and 50.86 ppb, respectively. In Petaling Jaya, the peak concentrations during HPE reached 68.8 ppb while the non-HPE peaks nearly doubled at 39.15 ppb in 2014. Similar trends were also found in Bandaraya Melaka in the same year with peak concentrations during HPE at 90.5 ppb, which is higher by 57.5 ppb than that those during the non-HPE periods.

The extremely high concentrations of O₃ during HPE can be attributed to the high quantity and efficiency of nitrogen oxide photochemical reactions. The results of the present study showed that NO₂ and NO concentrations were slightly higher during HPE than those during non-HPE even if only small differences were depicted by the diurnal plots. However, the findings of the present study differed with those of a past work for episodes of heavy pollution. In particular, by using the atmospheric chemistry model of the Weather Research and Forecasting, Feng et al. (2016) showed that high concentrations of aerosol can decrease photolytic frequencies and reduce O₃ concentrations. More concentrations of O₃ fluctuated in 2014 than 2013 due to the higher frequency incidences of

HPE. Several studies have reported that the rate of ozone formation is reduced by absorption and gas and particle scattering (Xing et al. 2017; Benas et al. 2013; Bian et al. 2017; Anger et al. 2016; Wang et al. 2016). In general, the reduction of O₃ formation is relatively more perceptible during HPE occurrences (Feng et al. 2016). Moreover, particles can affect the UV lights that penetrate directly to the ground, which then decreases the rate of O₃ formation (Zafonte et al. 1977; Liu et al. 1991; Lu and Khalil 1996).

However, some results of the present study differed from those of past work. For instance, relatively higher O₃ concentrations during HPE were recorded in Shah Alam, Petaling Jaya and Bandaraya Melaka. Similar findings were also obtained by Larson et al. (1984) in Pasadena, in which O₃ concentrations during heavy smog events were higher compared with clear days. These phenomena might have been affected by several reasons. The light scattering of particles may have reduced ozone formation rates, but this scenario depends on the wavelength of radiation λ and certain particles with varying geometrical shapes (Seinfeld and Pandis 2006). The three domains to depict radiation scattering are Rayleigh scattering (particle size is smaller than wavelength size), Mie scattering (particle size is similar to wavelength size) and geometric scattering (particle size is larger than wavelength size). Some particles found in the atmosphere have the ability to scatter radiation in all directions depending on their geometrical shape.

Undisturbed UV wavelength radiations can be represented by the existence of higher ambient temperature and significantly lower relative humidity during HPE compared with those during non-HPE. High photochemical rates during HPE can also slightly lower wind speed, an influencing factor of relatively calm conditions. Lal et al. (2000) reported that the dispersion and dilution of air pollution escalate in high wind speed conditions because of the relatively faster mixing process. Low wind speed also allows O₃ and other pollutions to build up into higher concentrations due to the low dispersion affect. In addition, according to Ghazali et al. (2010), wind speeds of less than 3 m/s can provide suitable conditions for O₃ accumulation. Higher O₃ precursors can increase O₃ concentrations with sufficient incoming solar radiation. As depicted by the case of Petaling Jaya, O₃ concentrations were higher during HPE in 2013 than 2014, which suggests that even if particles undergo light scattering, O₃ formation can still happen if high concentrations of O₃ precursors exist in the atmosphere. The concentrations of PM₁₀ also shows fluctuation with a higher amount of particulates during HPE compared with non-HPE.

The relations of O₃, NO₂ and NO concentrations during HPE and non-HPE were further explored by obtaining the O₃ photochemistry reactions rate. Jenkin and Clemitshaw (2000) found that the behaviour of NO and NO₂ was highly coupled because of rapid inter-conversion. Thus, in the

Table 3 Details on the 2013 and 2014 HPE in Malaysia

Descriptions	2013	2014
Month (no. of effected locations)	June (26) July (4)	February (1) March (15) April (1) June (3) July (17) August (2) September (3) October (4)
Total occurrence	30	46
Max. recorded API (location)	335 (Port Dickson)	358 (Klang)

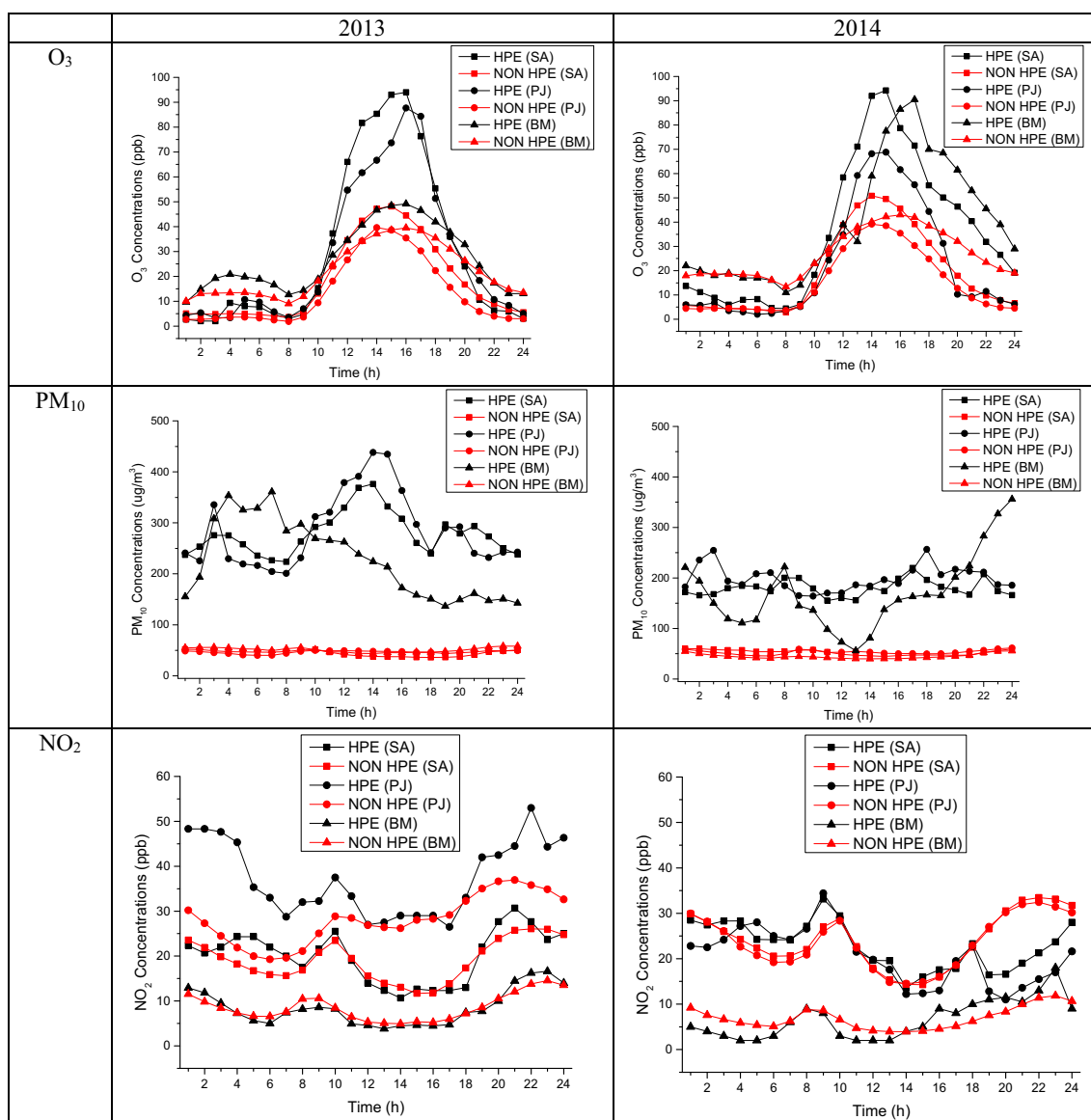


Fig. 2 Diurnal plots of pollutants and meteorological parameters during HPE and non-HPE

absence of competing inter-conversion reactions at the ground level, the photostationary state of the O_3 , NO and NO_2 relations subsequently relies on NO_2 photolysis (J_{NO_2}) and NO titration (K_3), the reactions rates of which can be depicted in a timescale over a few minutes (Han et al. 2011). The ratios of J_{NO_2}/k_3 fluctuated throughout the day given the varied daily concentrations of O_3 , NO_2 and NO. The average diurnal variations of J_{NO_2}/k_3 ratios during HPE and non-HPE are illustrated in Fig. 3. The figure also shows that the values of diurnal variation of J_{NO_2}/k_3 differ from one other, a finding similar found by Han et al. (2011) at Tianjin, China.

Theoretically, the value of (J_{NO_2}/k_3) is supposed to be zero because of the absence of photochemical reactions. However, the background O_3 concentration in the atmosphere leads to the existence of a minimal mixing ratio during HPE

(i.e. from 1 to 9 ppb). The trend started to increase and reached the maximum at 2.00 p.m. during non-HPE and 3.00 p.m. during HPE in 2013 and 2014. However, in Shah Alam, the J_{NO_2}/k_3 value increased to 20 ppb at 7 p.m. The differences in the J_{NO_2}/k_3 values were used as an indicator of O_3 photostationary state, and subsequently, for the difference between the rates of NO_2 photolysis and NO titrations (Clapp and Jenkin 2001). Positive differences in J_{NO_2}/k_3 depict O_3 accumulation, whereas negative J_{NO_2}/k_3 values indicate O_3 destruction.

Variation in ozone concentration with meteorological parameters

The general trend for the selected locations in this study shows an increase in temperature during HPE. The

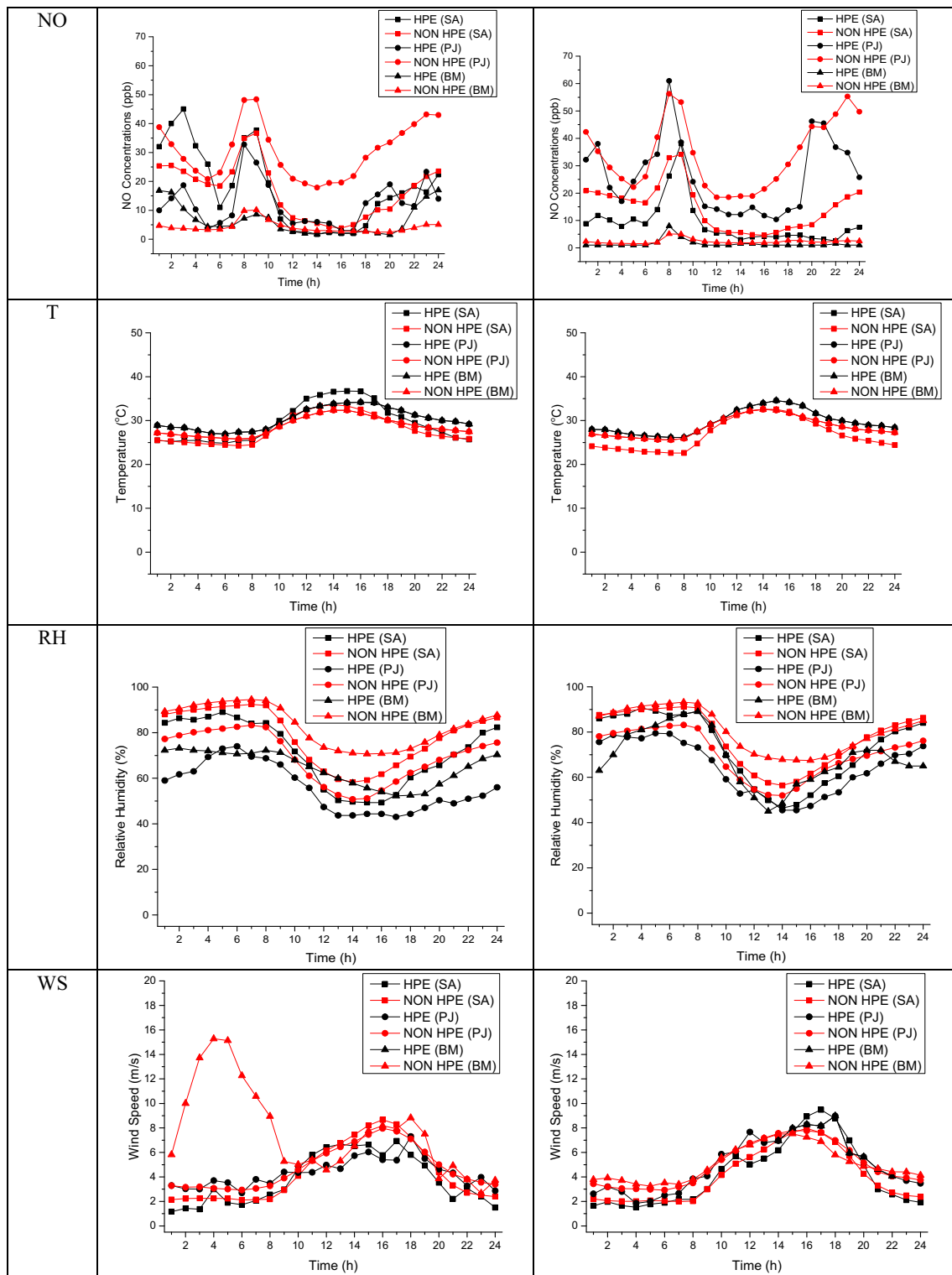


Fig. 2 (continued)

increase in temperature (heat) from biomass burning favours the increase of ozone concentrations because of the relatively higher photochemical reactions (Hauglustaine et al. 2001). This finding is supported by the condition in

which temperature photochemically influences the speed and amount of ozone production (Punithavathy et al. 2015). The ozone concentration during HPE accords with the existence of higher aerosols that absorb relatively more

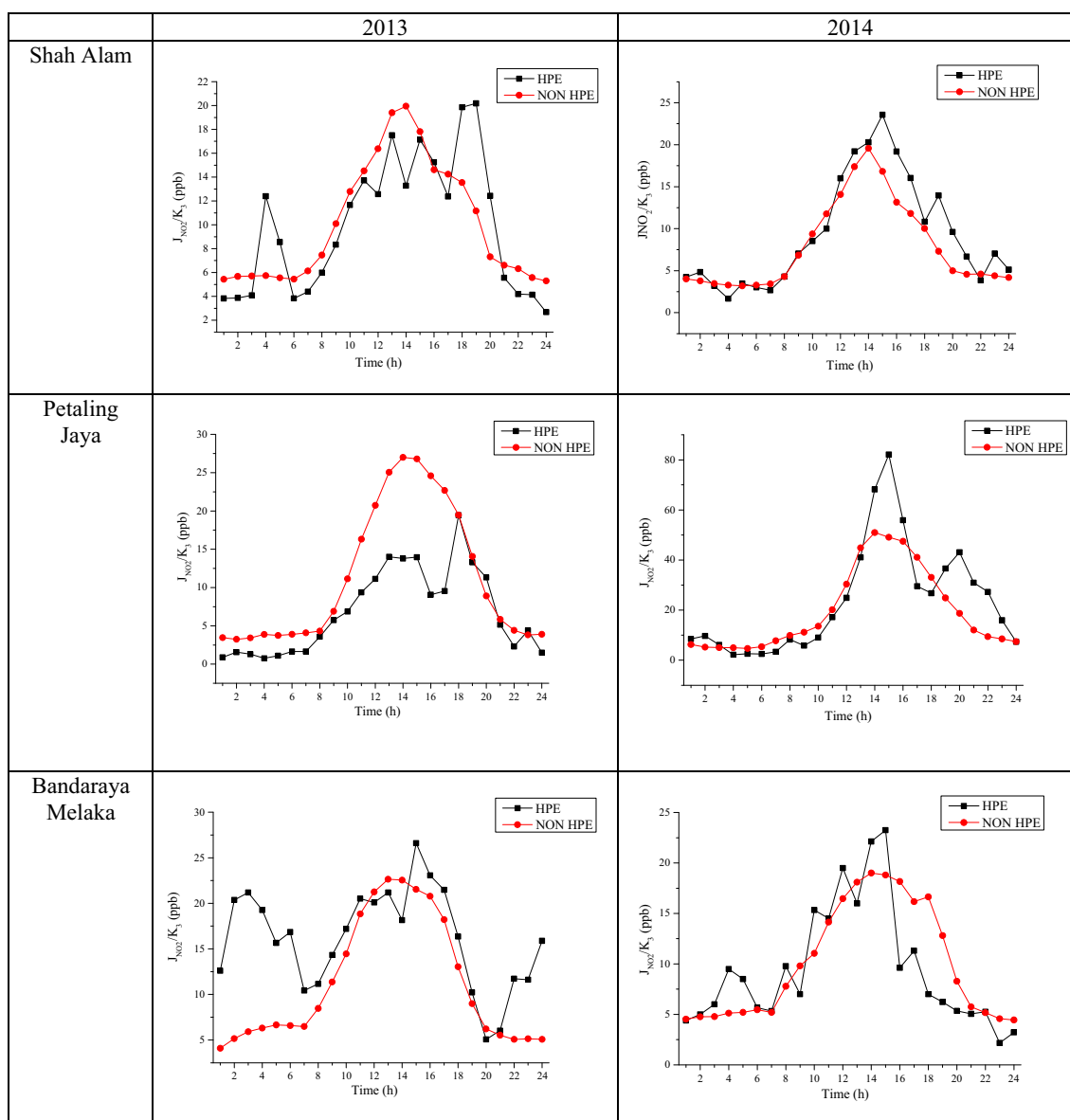


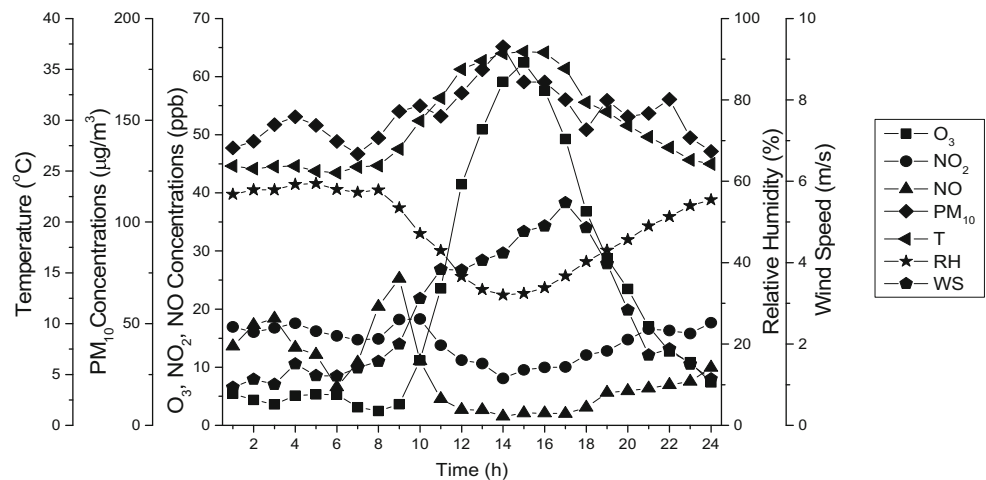
Fig. 3 Diurnal variations of average j_{NO_2}/k_3 ratio during HPE and non-HPE for 2013 and 2014

heat and the subsequent increase in earth temperature and ozone formation. Moreover, relative humidity affects ozone production because the photolysis of the ozone and the production of the excited oxygen atom both lead to the increase of hydroxyl radicals. Hydroxyl radicals can be oxidized and contribute to the production of ozone in the atmosphere (Lal et al. 2000; Saxena and Ghosh 2011), and this phenomenon can be attributed to the decrease in humidity at the time when ozone concentration started to increase in the selected urban locations. On this basis, the concentration of ozone was higher when the relative humidity was lower because more hydroxyl radicals were converted into ozone.

The concentration of ozone during night-time in all locations did not reach zero, and this condition can be explained

by the lifetime of the ozone in the lower troposphere (i.e. approximately 4–5 days to 1–2 weeks, but not by seasonal changes). Accordingly, the finding of the present work supports that from Naja et al. (2003) who explained that a new boundary layer is formed above the earth surface as the earth cools at night-time, and this air layer with fresh emissions isolates some of the pollutants observed from the previous day. The fresh emissions of pollutants are likely trapped below the newly formed boundary layer, and it is responsible for the detection of ozone during night-time (Saxena and Ghosh 2011). The diurnal plot of NO_2 and NO in this study also showed great fluctuations during HPE compared with non-HPE. The concentrations of NO_2 and NO were lower when the concentration of ozone was higher.

Fig. 4 Composite diurnal plot of air pollutants and meteorological parameters during HPE in Shah Alam



In summary, temperature and humidity both increased during HPE in all the selected locations. This finding is similar to that of Chan and Kwok (2001) who reported that the rise in temperature and humidity favours the formation of ground-level ozone. Slower wind speed is associated with the accumulation of ozone and the eventual rise in the concentration of ozone. However, as shown by the results for all the locations, a relatively higher ozone concentration exists at the time range when wind speed is higher.

Comparison of pollutants in different urban locations

The diurnal plots of pollutants and meteorological parameters during HPE and non-HPE in Shah Alam and Petaling Jaya are shown in Figs. 4 and 5, respectively. As depicted by the trends, the concentration of ozone is higher during HPE than that during non-HPE in 2013 and 2014. The trend for ozone fluctuation differed in the case of Bandaraya Melaka (Fig. 6) given the high ozone from 12 a.m. to 10 a.m., followed by a slow rise in the afternoon, and finally, a decrease towards the evening. This trend can be attributed

to the relatively higher relative humidity that increases the conversion of hydroxyl radicals and subsequently acts as the ozone precursor.

The concentrations of PM₁₀ also showed clear fluctuations with high concentrations during HPE than those during non-HPE in all the urban sites. This finding can be attributed to the HPE that is associated with the incremental particulate matters in urban areas that originate from biomass burning (Abas et al. 2004; Chow et al. 1992), fossil fuel combustion (Afroz et al. 2003) and industrial activities (Rahman et al. 2015; Dominick et al. 2012; Karar et al. 2006; Afroz et al. 2003). The concentrations of NO₂ and NO also show clear fluctuations in all locations. Both concentrations were higher during HPE in most locations than those during non-HPE. For instance, the NO₂ concentrations in Shah Alam and Petaling Jaya were relatively higher from 1.00 a.m. to 8.00 a.m. during HPE, but the opposite was observed in Bandaraya Melaka (i.e. NO₂ concentrations were relatively lower during HPE in 2013 and 2014). This finding implies that the fluctuational characteristic of pollutants during HPE varies depending on the location given all other factors considered.

Fig. 5 Composite diurnal plot of air pollutants and meteorological parameters during HPE in Petaling Jaya

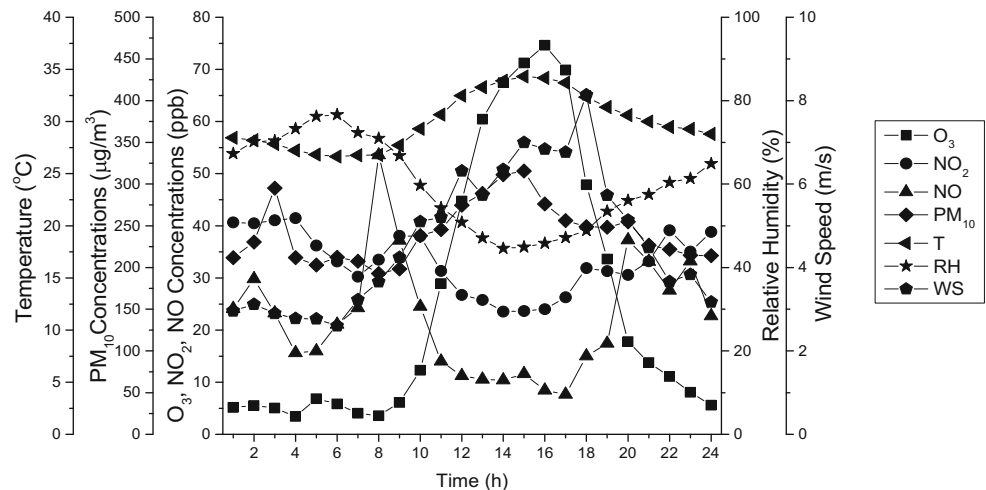
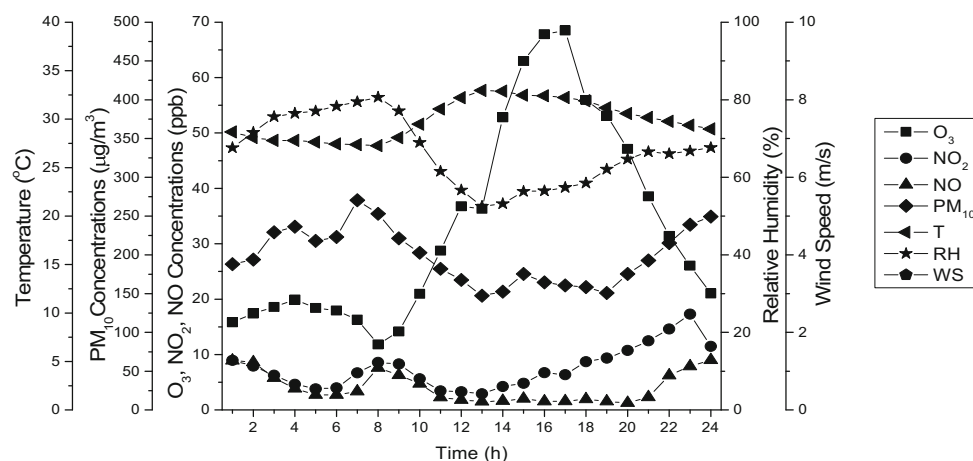


Fig. 6 Composite diurnal plot of air pollutants and meteorological parameters during HPE in Bandaraya Melaka



A higher temperature during HPE was observed in all locations than during non-HPE. The increase in temperature was associated with the incremental heat of the haze phenomena, in which airborne particulates in the atmosphere either absorbed/retained heat or affected the scattering of light into earth depending on the particle sizes. This finding is similar to the studies conducted by Zhang et al. (2017) in which a drastic change to the type, shape and size of aerosol particles during haze significantly affect the scattering ability and absorbing capacity of solar spectral radiation. The aerosol particles can

directly modulate radiation energy in the atmosphere by scattering and absorbing solar/terrestrial radiation (Tomasi et al. 2007) to later affect atmospheric heating rate and stability.

The results are in accordance with the study conducted in Beijing on January 2013. The mean absorption of sunlight by aerosols was extremely strong, although haze particles in general can strongly scatter sunlight (Bi et al. 2014). Therefore, the increase in temperature during HPE may have been caused by the presence of aerosol (e.g. PM₁₀) and contribute to the fluctuations in ozone concentration. The values of relative

Table 4 Pearson correlation of air pollutants and meteorological parameters during HPE and non-HPE

Station	Parameter	HPE							non-HPE							
		O ₃	PM ₁₀	NO ₂	NO	T	RH	WS	O ₃	PM ₁₀	NO ₂	NO	T	RH	WS	
Shah Alam	O ₃ (ppb)	1.00							1.00							
	PM ₁₀ (µg/m ³)	0.81	1.00						-0.82	1.00						
	NO ₂ (ppb)	-0.93	-0.69	1.00					-0.68	0.53	1.00					
	NO (ppb)	-0.78	-0.53	0.74	1.00				-0.84	0.84	0.48	1.00				
	T (°C)	0.97	0.84	-0.88	-0.74	1.00			0.96	-0.75	-0.58	-0.81	1.00			
	RH (%)	-0.96	0.87	0.87	0.77	-0.99	1.00		-0.97	0.77	0.57	0.82	-0.99	1.00		
	WS (m/s)	0.91	0.72	-0.84	-0.71	0.94	-0.94	1.00	0.97	-0.84	-0.63	-0.83	0.95	-0.95	1.00	
Petaling Jaya	O ₃ (ppb)	1.00							1.00							
	PM ₁₀ (µg/m ³)	0.79	1.00						0.02	1.00						
	NO ₂ (ppb)	-0.86	-0.64	1.00					-0.35	0.57	1.00					
	NO (ppb)	-0.69	-0.59	0.45	1.00				-0.69	0.38	0.61	1.00				
	T (°C)	0.95	0.80	-0.79	-0.62	1.00			0.96	0.23	-0.12	-0.56	1.00			
	RH (%)	-0.90	-0.75	0.77	0.52	-0.98	1.00		-0.94	-0.26	0.12	0.55	-0.99	1.00		
	WS (m/s)	0.88	0.66	-0.77	-0.49	0.91	-0.93	1.00	0.95	0.07	-0.16	-0.54	0.96	-0.94	1.00	
Bandaraya Melaka	O ₃ (ppb)	1.00							1.00							
	PM ₁₀ (µg/m ³)	-0.76	1.00						-0.73	1.00						
	NO ₂ (ppb)	-0.05	0.28	1.00					-0.56	0.88	1.00					
	NO (ppb)	-0.68	0.61	0.49	1.00				-0.49	0.27	0.38	1.00				
	T (°C)	0.87	-0.86	-0.17	-0.63	1.00			0.96	-0.62	-0.44	-0.38	1.00			
	RH (%)	-0.81	0.86	0.11	0.51	-0.98	1.00		-0.97	0.63	0.44	0.39	-0.99	1.00		
	WS (m/s)	-	-	-	-	-	-	-	0.13	-0.46	-0.70	-0.36	-0.09	0.09	1.00	

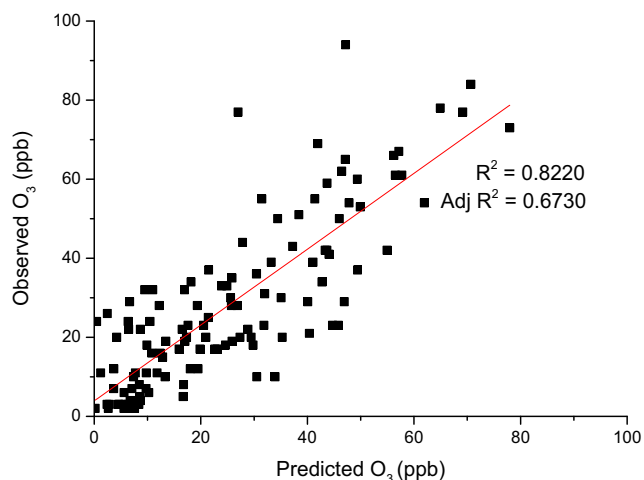


Fig. 7 Scatter plot of observed and predicted O₃ concentration during 2013 and 2014 HPE

humidity of Bandaraya Melaka, Petaling Jaya and Shah Alam were lower during HPE than those during non-HPE. The observed decreasing trend could be due to the increase in hydroxyl radicals that were formed because of the relatively higher temperature during HPE. Although some data were not available for Bandaraya Melaka, the abovementioned factor can explain the fluctuating pollutant concentrations and the ability to dilute/disperse or accumulate pollutants in the study areas. As shown in Figs. 4, 5 and 6, wind speed was higher during HPE than during non-HPE in 2014, and a particular reason may be that more HPE events occurred that particular year.

Table 4 shows the correlation of all ozone-related pollutants observed in the study sites. The correlations of PM₁₀ with ozone during HPE were positive for Shah Alam and Petaling Jaya with 0.81 and 0.79, whereas a negative correlation (−0.76) was derived for Bandaraya Melaka. However, the correlations of PM₁₀ with ozone were negative in the study locations during non-HPE except for Petaling Jaya with 0.02. The temperature factor exhibited a strong positive correlation with ozone in all locations during HPE and non-HPE, and the highest is for Shah Alam with 0.97. Thus, temperature can significantly affect the concentration of ozone, and this finding is similar to that found by Punithavathy et al. (2015).

In summary, relative humidity had a strong negative correlation with ozone. In this study, the highest derived values were for Shah Alam (−0.96) in 2013 and Shah Alam (−0.97) and Bandaraya Melaka (−0.97) in 2014, and both findings accord with the study results of Tong et al. (2017) and Mohamad

Hashim et al. (2018). Moreover, wind speed had a strong positive correlation in all locations, and the highest values were all for 2014. The data for the study were derived by referring to the composite diurnal plots of air pollutants and meteorological parameters during HPE in Shah Alam, Petaling Jaya and Bandaraya Melaka in 2013 and 2014 (Figs. 4, 5 and 6).

Best prediction model

The O₃ concentrations predicted by the multiple linear regression (MLR) models are plotted against the observed O₃ concentrations presented in Fig. 7. Table 5 shows summarized results of the O₃ best-fit equation which was developed for the selected urban areas with a 2-year study period. The modelling obtained an adjusted R^2 of 0.6730, which implies that the parameters used for the study had a significant positive relationship. The finding also shows that the variables can explain the variations in O₃ during HPE at the rate of 67.30% for both 2013 and 2014. The range of the variance inflation factor was below 10 (1.504–8.326) and thus in the acceptable range for O₃ next-hour prediction. The Durbin–Watson test result was 2.588, a value that can be interpreted as having no autocorrelation but essentially leans to the negative.

Conclusion

A clear fluctuation exists in the concentrations of pollutants during HPE in the studied urban sites, as shown by the diurnal plots. The concentrations of ozone were higher during HPE than those during non-HPE, and they were affected by the relatively higher temperatures and lower relative humidity, which generally accords with the findings for HPE. Thus, an HPE occurrence can lead to the increase in ozone concentration. Moreover, the temperature in the study area was higher during HPE and subsequently derived a strong positive correlation with ozone ($r = 0.87–0.97$) due to the presence of aerosols, whereas relative humidity exhibited a strong negative correlation in the study sites. Wind speed also showed a strong positive correlation in all of the study sites except Bandaraya Melaka ($r = 0.13$). The result indicates that the fluctuations observed during HPE vary depending on the urban location. The ozone best-fit equation obtained an R^2 of 0.6730. The parameters used in the study have a significant positive relationship with ozone prediction.

Table 5 Summary of models for O₃ concentration in urban areas during 2013 and 2014 HPE

Models	Adjusted R^2	Range of VIF	Durbin-Watson
$O_3(t+1) = -16.533 + 0.690O_3 + 0.029 PM_{10} - 0.137NO_2 - 0.009NO + 0.664 T - 0.036RH + 0.875WS$	0.6730	1.504–8.326	2.588

Acknowledgements The authors would like to express their great gratitude to the Department of Environment of Malaysia for the data provided for this research and the Universiti Sains Malaysia for the research funding.

Funding information This study was funded under grant 1001/PAWAM/814278.

References

- Abas MR, Oros DR, Simoneit BRT (2004) Biomass burning as the main source of organic aerosol particulate matter in Malaysia during haze episodes. *Chemo* 55:1089–1095
- Abdullah AM, Samah MAA, Jun TY (2012) An overview of the air pollution trend in Klang Valley, Malaysia. *Open Environ Sci* 6:13–19
- Abdul-Wahab SA, Bakheit CS, Al-Alawi SM (2005) Principal component and multiple regression analysis in modelling of ground-level ozone and factors affecting its concentrations. *Environ Model Soft* 20:1263–1271
- Afroz R, Hassan MN, Ibrahim NA (2003) Review of air pollution and health impacts in Malaysia. *Environ Res* 92:71–77
- Alghamdi MA, Khoder M, Harrison RM, Hyvärinen A-P, Hussein T, Al-Jeelani H, Abdelmaksoud AS, Goknil MH, Shabbaj II, Almeahadi FM, Lihavainen H, Kulmala M, Hämeri K (2014) Temporal variations of O₃ and NO_x in the urban background atmosphere of the coastal city Jeddah, Saudi Arabia. *Atmos Environ* 94:205–214
- Amil N, Latif MT, Khan MF, Mohamad M (2016) Seasonal variability of PM_{2.5} composition and sources in the Klang Valley urban-industrial environment. *Atmos Chem Phys* 16:5357–5381
- Anger A, Dessens O, Xi F, Barker T, Wu R (2016) China's air pollution reduction efforts may result in an increase in surface ozone levels in highly polluted areas. *Ambio* 45:254–265
- Awang M, Jaafar AB, Abdullah AM, Ismail M, Hassan MN, Abdullah R, Noor H (2000) Air quality in Malaysia: impacts, management issues and future challenges. *Resp* 5:183–196
- Awang NR, Ramli NA, Yahaya AS, Elbayoumi M (2015) Multivariate methods to predict ground level ozone during daytime, nighttime, and critical conversion time in urban areas. *Atmos Poll Res* 6:726–734
- Awang NR, Elbayoumi M, Ramli NA, Yahaya AS (2016) Diurnal variations of ground-level ozone in three port cities in Malaysia. *Air Qual Atmos Health* 9(1):25–39
- Banan N (2013) Characteristics of surface ozone concentrations at stations with different backgrounds in the Malaysian Peninsula. *Aerosol Air Qual Res* 13:1090–1106. <https://doi.org/10.4209/aaqr.2012.09.0259>
- Benas N, Mourtzanou E, Kouvarakis G, Bais A, Mihalopoulos N, Vardavas I (2013) Surface ozone photolysis rate trends in the Eastern Mediterranean: modeling the effects of aerosols and total column ozone based on Terra MODIS data. *Atmos Environ* 74:1–9
- Bi J, Huang J, Hu Z, Holben BN, Guo Z (2014) Investigating the aerosol optical and radiative characteristics of heavy haze episodes in Beijing during January of 2013. *J Geophys Res: Atmos* 119(16):9884–9900
- Bian H, Han S, Tie X, Sun M, Liu A (2017) Evidence of impact of aerosols on surface ozone concentration in Tianjin, China. *Atmos Environ* 41:4672–4681
- Bo H, Yuesi W, Guangren L (2010) Properties of ultraviolet radiation and the relationship between ultraviolet radiation and aerosol optical depth in China. *Atmos Res* 98:297–308
- Camalier L, Cox W, Dolwick P (2007) The effects of meteorology on ozone in urban areas and their use in assessing ozone trends. *Atmos Environ* 41:7127–7137
- Chan LY, Kwok WS (2001) Roadside suspended particulates at heavily trafficked urban sites of Hong Kong—seasonal variation and dependence on meteorological conditions. *Atmos Environ* 35:3177–3182
- Chooi TK, San LH, Jafri, MZM (2014) Observed atmospheric total column ozone distribution from SCIAMACHY over Peninsular Malaysia Paper presented at the IOP Conference Series: Earth and Environmental Science
- Chow JC, Watson JG, Lowenthal DH, Solomon PA, Magliano KL, Ziman SD, Richards LW (1992) PM₁₀ source apportionment in California's San Joaquin Valley. *Atmos Environ Part A General Topics* 26(18):3335–3354
- Clapp LJ, Jenkin ME (2001) Analysis of the relationship between ambient levels of O₃, NO₂ and NO as a function of NO_x in the UK. *Atmos Environ* 35:6391–6405
- Dominick D, Juahir H, Latif MT, Zain SM, Aris AZ (2012) Spatial assessment of air quality patterns in Malaysia using multivariate analysis. *Atmos Environ* 60:172–181
- Feng T, Bei N, Huang RJ, Cao J, Zhang Q, Zhou W, Li G (2016) Summertime ozone formation in Xi'an and surrounding areas, China. *J Atmos Chem Phys* 16:4323–4342
- Ghazali NA, Ramli NA, Yahaya AS, Yusof NFF, Sansuddin N, Al Madhoun WA (2010) Transformation of nitrogen dioxide into ozone and prediction of ozone concentrations using multiple linear regression techniques. *Environ Monit Assess* 165(1–4):475–489
- Gong X, Hong S, Jaffe AD (2017) Ozone in China: spatial distribution and leading meteorological factors controlling O₃ in 16 Chinese cities. *Aerosol Air Qual Res*. <https://doi.org/10.4209/aaqr.2017.10.0368>
- Han S, Bian H, Feng Y, Liu A, Li X, Zeng F, Zhang X (2011) Analysis of the relationship between O₃, NO and NO₂ in Tianjin, China. *Aerosol Air Qual Res* 11(2):128–139
- Hauglustaine D, Emmons L, Newchurch M, Brasseur G, Takao T, Matsubara K, Dye J (2001) On the role of lightning NO_x in the formation of tropospheric ozone plumes: a global model perspective. *J Atmos Chem* 38:277–294
- Huang J, Minnis P, Chen B, Huang Z, Liu Z, Zhao Q, Ayers JK (2008) Long-range transport and vertical structure of Asian dust from CALIPSO and surface measurements during PACDEX. *J Geophys Res Atmos* 113(D23)
- IPCC (2007) Intergovernmental Panel on Climate Change. Climate Change 2007 - Mitigation of Climate Change: Working Group III contribution to the Fourth Assessment Report of the IPCC: Cambridge: Cambridge University Press
- Jenkin ME, Clemmitshaw KC (2000) Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer. *Atmos Environ* 34:2499–2527
- Karar K, Gupta AK, Kumar A, Biswas AK, Devotta S (2006) Statistical interpretation of weekday/weekend differences of ambient particulate matter, vehicular traffic and meteorological parameters in an urban region of Kolkata, India. *Indoor Built Environ* 15(3):235–245
- Khan MF, Latif MT, Saw WH, Amil N, Nadzir MSM (2016) Fine particulate matter in the tropical environment: monsoonal effects, source apportionment, and health risk assessment. *Atmos Chem Phys* 16:597–617
- Kumar A, Singh D, Singh BP, Singh M, Anandam K, Kumar K, Jain VK (2015) Spatial and temporal variability of surface ozone and nitrogen oxides in urban and rural ambient air of Delhi-NCR, India. *Air Qual Atmos Health* 8(4):391–399
- Lal S, Naja M, Subbaraya BH (2000) Seasonal variations in surface ozone and its precursors over an urban site in India. *Atmos Environ* 34(17):2713–2724
- Larson S, Cass G, Hussy K, Luce F (1984) Visibility model verification by image processing techniques, Final report to State of California Air Resources Board under agreement A2-077-32, Sacramento, CA
- Latif MT, Huey LS, Juneng L (2012) Variations of surface ozone concentration across the Klang Valley, Malaysia. *Atmos Environ* 61:434–445

- Li Z, Lee KH, Wang Y, Xin J, Hao WM (2010) First observation-based estimates of cloud-free aerosol radiative forcing across China. *J Geophys Res Atmos* 115. doi: <https://doi.org/10.1029/2009JD013306>
- Li W, Shao L, Shi Z, Chen J, Yang L, Yuan Q, Yan C, Zhang X, Wang Y, Sun J, Zhang Y, Shen X, Wang Z, Wang W (2014) Mixing state and hygroscopicity of dust and haze particles before leaving Asian continent. *J Geophys Res: Atmos* 119(2):1044–1059
- Liu JC, Peng RD (2018) Health effect of mixtures of ozone, nitrogen dioxide, and fine particulates in 85 US counties. *Air Qual Atmos Health*:1–14
- Liu SC, McKeen SA, Madronich S (1991) Effect of anthropogenic aerosols on biologically active ultraviolet radiation. *Geophys Res Letters* 18(12):2265–2268
- Liu SK, Cai S, Chen Y, Xiao B, Chen P, Xiang XD (2016) The effect of pollutional haze on pulmonary function. *J Tho Dis* 8(1):E41
- Lu Y, Khalil MAK (1996) The distribution of solar radiation in the earth's atmosphere: the effects of ozone, aerosols and clouds. *Chemos* 32(4):739–758
- McNaught AD, Wilkinson A (1997) IUPAC. In: Compendium of chemical terminology, 2nd edn. (the “Gold Book”). Blackwell Scientific Publications, Oxford
- Mohamad Hashim NI, Mohamed Noor N, Yusof SY (2018) Temporal characterisation of ground-level ozone concentration in Klang Valley. *E3S Web of Conferences* 34:02047
- Naja M, Lal S, Chand D (2003) Diurnal and seasonal variabilities in surface ozone at a high altitude site Mt Abu in India. *Atmos Environ* 37:4205–4215
- Norela S, Saidah MS, Mahmud M (2013) Chemical composition of the haze in Malaysia 2005. *Atmos Environ* 77:1005–1010
- Punithavathy IK, Vijayalakshmi S, Jeyakumar SJ (2015) Assessment of ground-level ozone and its variability with meteorological parameters at Karaikal, India. *Uni J Environ Res Tech* 5(5)
- Rahman SRA, Ismail SNS, Raml MF, Latif MT, Abidin EZ, Praveena SM (2015) The assessment of ambient air pollution trend in Klang Valley, Malaysia. *World Environ* 5(1):1–11
- Rai R, Rajput M, Agrawal M, Agrawal SB (2011) Gaseous air pollutants: a review on current and future trends of emissions and impact on agriculture. *J Scie Res* 55(771):1
- Ramanathan V, Crutzen PJ, Lelieveld J, Mitra AP, Althausen D, Anderson J, Valero FPJ (2001) Indian Ocean experiment: an integrated analysis of the climate forcing and effects of the great Indo-Asian haze. *J Geophys Res: Atmos* 106:2156–2202. <https://doi.org/10.1029/2001JD900133>
- Reid JS, Hobbs PV, Ferek RJ, Blake DR, Martins JV, Dunlap MR, Liousse C (1998) Physical, chemical, and optical properties of regional hazes dominated by smoke in Brazil. *J Geophys Res Atmos* 103(D24):32059–32080
- Saxena P, Ghosh C (2011) Variation in the concentration of ground level ozone at selected sites in Delhi. *Int J Environ Sci* 1(7):1899–1911
- Seinfeld J, Pandis SN (2006) Atmospheric chemistry and physics: from air pollution to climate change, 2nd edn. John Wiley & Sons, Inc, New Jersey
- Sicard P, Coddeville P, Claude JC (2009) Near-surface ozone levels and trends at rural stations in France over the 1995–2003 period. *Environ Monit Assess* 156(1–4):141–157
- Tomasi C, Vitale V, Lupi A, Di Carmine C, Campanelli M, Herber A, Radionov V (2007) Aerosols in polar regions: a historical overview based on optical depth and in situ observations. *J Geophys Res Atmos* 112(D16)
- Tong L, Zhang H, Yu J, He M, Xu N, Zhang J, Qian F, Feng J, Xiao H (2017) Characteristics of surface ozone and nitrogen oxides at urban, suburban and rural sites in Ningbo, China. *Atmos Res* 187:57–68
- Toro R, Seguel RJ (2015) Ozone, nitrogen oxides, and volatile organic compounds in a central zone of Chile. *Air Qual Atmos Health* 8(6):545–557
- Toro RA, Donoso CS, Seguel RA, Morales RG, Leiva MA (2014) Photochemical ozone pollution in the Valparaiso Region, Chile. *Air Qual Atmos Health* 7(1):1–11
- Wang J, Allen DJ, Pickering KE, Li Z, He H (2016) Impact of aerosol direct effect on East Asian air quality during the EAST-AIRE campaign. *J Geophys Res Atmos* 121(11):6534–6554
- Wolff GT, Lioy PJ (1978) An empirical model for forecasting maximum daily ozone levels in the Northeastern U.S. *J Air Poll Control Assoc* 28(10):1034–1038
- Xing J, Wang J, Mathur R, Wang S, Sarwar G, Pleim J, Hogrefe C, Zhang Y, Jiang J, Wong DC, Hao J (2017) Impacts of aerosol direct effects on tropospheric ozone through changes in atmospheric dynamics and photolysis rates. *Atmos Chem Phys* 17:9869–9883
- Yi J, Prybutok VR (1996) A neural network model forecasting for prediction of daily maximum ozone concentration in an industrialized urban area. *Environ Poll* 92(3):349–357
- Zafonte L, Rieger PL, Holmes JR (1977) Nitrogen dioxide photolysis in the Los Angeles atmosphere. *Environ Sci Technol* 11(5):483–487
- Zhang M, Ma Y, Gong W, Wang L, Xia X, Che H, Liu B (2017) Aerosol radiative effect in UV, VIS, NIR, and SW spectra under haze and high-humidity urban conditions. *Atmos Environ* 166:9–21. <https://doi.org/10.1016/j.atmosenv.2017.07.006>
- Zhao H, Wang W, Liu R, Zhou B (2015) Investigation of ground-level ozone and high-pollution episodes in a megacity of Eastern China. *Pub Lib Sci (PLoS)* 10(6):e0131878