



Short communication

Time effects of high particulate events on the critical conversion point of ground-level ozone



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ARTICLE INFO

Keywords:

Ozone production
Anthropogenic sources
Ozone precursor
Photochemical reaction
Particulate matter

ABSTRACT

Particulate matter (PM), especially those with an aerodynamic particle size of less than 10 μm (PM_{10}), is typically emitted from transboundary forest fires. A large-scale forest fire may contribute to a haze condition known as a high particulate event (HPE), which has affected Southeast Asia, particularly Peninsular Malaysia, for a long time. Such event can alter the photochemical reactions of secondary pollutants. This work investigates the influence of PM on ground-level ozone (O_3) formation during HPE. Five continuous air quality monitoring stations from different site categories (i.e., industrial, urban and background) located across Peninsular Malaysia were selected in this study during the HPEs in 2013 and 2014. Result clearly indicated that O_3 concentrations were significantly higher during HPE than during non-HPE in all the sites. The O_3 diurnal variation in each site exhibited a similar pattern, whereas the magnitudes of variation during HPE and non-HPE differed. Light scattering and atmospheric attenuation were proven to be associated with HPE, which possibly affected O_3 photochemical reactions during HPE. Critical conversion time was used as the main determining factor when comparing HPE and non-HPE conditions. A possible screening effect that resulted in the shifting of the critical transformation point caused a delay of approximately of 15–30 min. The shifting was possibly influenced by the attenuation of sunlight in the morning during HPE. A negative correlation between O_3 and PM_{10} was observed during the HPE in Klang in 2013 and 2014, with -0.87 . Essentially, HPE with a high PM concentration altered ground-level O_3 formation.

1. Introduction

Atmospheric haze is typically associated with reduced visibility due to an increase in aerosol loading, which can substantially impact the radiative balance of the direct reflection of the Earth (or indirect reflection due to cloud formation) and the absorption of incoming solar radiation (Seinfeld and Pandis, 2006). In Southeast Asia, atmospheric haze, which is commonly known as smoke haze due to its large-scale plumes or airborne pollutants, is associated with wildfires or biomass burning resulting from the open burning of agricultural residues, slash-and-burn practices, and forest fires (Velasco and Rastan, 2015; Ahmed et al., 2016). In addition to biomass burning, atmospheric haze episodes have also been attributed to anthropogenic sources, which are mainly contributed by growing urbanisation and expanding economic

activities. In Malaysia, atmospheric haze is predominantly associated with surges in the concentration of ambient particulates (Rahman, 2013). Accordingly, the term ‘high particulate event (HPE)’ is used in the current study to refer to atmospheric haze episodes due to particulates.

The physical, chemical and optical properties of HPE can have physical, biological and economic effects on ecosystems, human health and water budget (Xu et al., 2015; Zhou et al., 2015). Severe and long-term HPE can indirectly affect the efficiency of vegetative photosynthesis (Xu et al., 2015) given that HPE can reduce atmospheric visibility by 20%–90% (Wang, 2003). The deposition of water-insoluble aerosols on plant leaves may reduce vegetative photosynthesis by up to 35% (Bergin et al., 2001), intensify crop yield and possibly increase the greenhouse effect. Scientific evidence has also shown a strong

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association between HPE and certain health problems, such as premature mortality, cardiovascular and respiratory diseases and lung cancer (Olmo et al., 2011). The combination of prolonged dry weather in Southeast Asia and the widespread anthropogenic land-clearing fires in central Sumatera reduced visibility and air quality in Peninsular Malaysia, including Singapore, during an extensive and large-scale HPE in June 2013. During this event, more than 600 schools in southern Peninsular Malaysia were closed because the Air Pollution Index (API) exceeded the hazardous point of 300. At the peak of the event, two districts were placed under a state of emergency because the API reached 700 (DoE, 2013; Rahman, 2013).

The adverse impacts of the 2013 HPE on the air quality of countries along the Strait of Malacca (i.e. Malaysia, Singapore and Indonesia) have been reported in many studies in terms of primary observations during the event (Othman et al., 2014) and direct impacts on ecosystems, environmental outcomes and economic losses (Velasco and Rastan, 2015). In addition, several studies have investigated the characteristics and composition of particulates (Fujii et al., 2015; Zhou et al., 2015; Ahmed et al., 2016), the link between aerosol optical depth and free space optics (Maghami et al., 2015; Malik and Singh, 2015), transboundary smoke–haze dispersion (Reid et al., 2013) and numerical modelling (Reddington et al., 2014).

Ozone (O_3) exists as a secondary pollutant in the lower atmosphere, where its formation and destruction highly depend on ultraviolet (UV) radiation and the intensity of its precursors, such as nitrogen oxides (NO_x) (Ainsworth et al., 2012; Hassan et al., 2013; Alghamdi et al., 2014). Aside from being a secondary pollutant that requires UV light to complete its photochemical reactions, O_3 is a noxious air pollutant and is recognised as the second most significant air pollutant in Malaysia (Rahman, 2013). O_3 is toxic to humans and vegetation at the ground level due to its capability to oxidise biological tissues (Brimblecombe, 2009; Pugliese et al., 2014). The transformational characteristics of O_3 during HPE are crucial for understanding the role of this air pollutant in such event. HPE conditions may trigger high O_3 photochemical reactions, which intensify the impacts of HPE due to large increments of ambient particulates and O_3 .

Studies on O_3 formation and variation are regarded as complex because of various possible precursors, photochemical processes, sunlight intensities and meteorological factors (Chattopadhyay and Chattopadhyay, 2011; Toh et al., 2013). Different approaches, including direct observation (Azmi et al., 2010) and empirical modelling (Sousa et al., 2007; Ozbay et al., 2011; Dominick et al., 2012), have been utilised to explain these processes. Awang et al. (2015) introduced the use of critical transformational time (CCT), which is determined based on the photochemical reactions of O_3 formation. CCT is obtained based on O_3 critical transformational point (CCP), which is a point when the rate of nitrogen dioxide (NO_2) photolysis is higher than that of nitric oxide (NO) titration, thereby resulting in the accumulation of O_3 concentration.

The current study clearly indicates that CCT is crucial to daily O_3 transformation, and this period can better represent O_3 variations than daytime. Moreover, after analysing 12 years of O_3 transformation and its precursor monitoring records, Awang et al. (2016) found that CCT in Malaysia typically occurs between 8 a.m. and 11 a.m. during non-HPE. However, the finding emphasised that several changes might have occurred during CCP time due to changes in atmospheric conditions, surges in precursors or obstructions of UV intensity. HPE can alter a single or a mixture of O_3 photochemical ingredients; hence, understanding O_3 CCP during HPE may provide crucial evidence for O_3 transformational behaviour. Therefore, this study aims to further explore the possibilities of using CCP to explain O_3 production during HPE and to establish a possible relationship between gases and particulate pollutants.

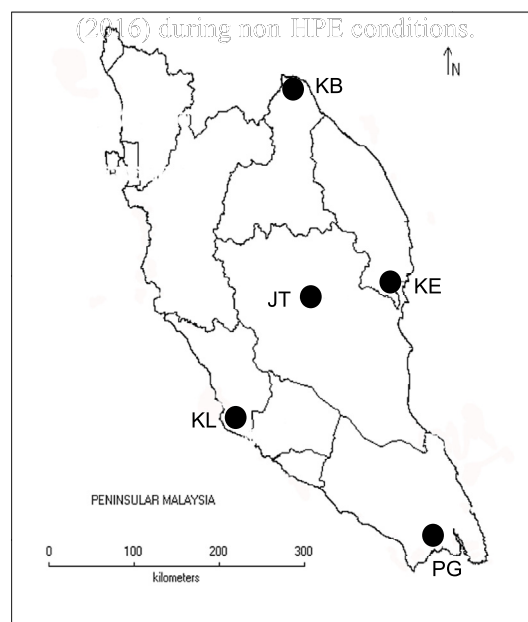


Fig. 1. Location of selected monitoring stations in Malaysia.

2. Methods

2.1. Location of sampling station

This study focused on the 2013 and 2014 HPEs. The duration of an HPE is determined based on API value because an HPE is considered to occur once the API value continuously exceeds 100 for 24 h. Five continuous air quality monitoring stations located across Peninsular Malaysia were selected in this study, as shown in Fig. 1. These stations were grouped into three categories, namely, industrial [Pasir Gudang (PG) and Kemaman (KE)], urban [Kota Bharu (KB) and Klang (KL)] and background [Jerantut (JT)], for HPE and non-HPE. The occurrence of an HPE for over 24 h was the main criterion for selecting the study areas, whereas the stations were chosen from among those included in Awang et al. (2016) to account for variations during non-HPE periods. The details of the occurrence period of HPE in 2013 and 2014 are provided in Table 1. The data collected was annual data in 2013 and 2014. Most of the selected HPE dates occurred in 2013, except for those in Klang, where the number of HPE hours was between 28 h and 112 h. Meanwhile, non-HPE data refer to the remaining data for that month of the year. All the selected stations are under a tropical climate characterised by a uniform high temperature ranging from 22 °C to 24 °C during nighttime and from 27 °C to 30 °C during daytime. The mean annual rainfall is 2670 mm (Ghazali et al., 2010; Md Yusof et al., 2010), and relative humidity ranges from 70% to 90%.

2.2. Data collection

The hourly secondary monitoring records of O_3 , particulate matter (PM) with an aerodynamic diameter less than 10 μm (PM_{10}), NO , NO_2 concentrations and meteorological parameters (i.e. wind speed, WS; temperature, T and relative humidity, RH) were obtained from the Air Quality Division, Department of Environment (DoE), Malaysia. These variables were selected based on their relationship with O_3 production (Clapp and Jenkin, 2001; Seinfeld and Pandis, 2006).

Hourly O_3 concentration was monitored using the Model 400E UV Absorption Ozone Analyser (DoE, 2010). This analyser applies the Beer–Lambert law, which is based on the internal electronic resonance of O_3 molecules with a UV light absorption of 254 nm in measuring low ranges of O_3 concentration in ambient air (Ghazali et al., 2010; Mohammed et al., 2013). Changes in ambient NO_2 and NO

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