Assessment of Gaseous Criteria Pollutants in Bangkok Metropolitan Region, Thailand

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Abstract. Analysis of gaseous criteria pollutants in Bangkok Metropolitan Region (BMR), Thailand, during 2010 to 2014 reveals that while the hourly concentrations of CO, SO₂ and NO₂ were mostly within the National Ambient Air Quality Standards (NAAQs) of Thailand; however, the hourly concentrations of O₃ frequently exceeded the standard. The results reveal that the problem of high O₃ concentration continuously persisted in this area. The O₃ photolytic rate constant (j₁) for BMR calculated based on assuming photostationary state (ranged from 0.008 to 0.013 s⁻¹) which is similar to the calculated j₁ using the NCAR TUV model (0.021±0.0024 s⁻¹). Interconversion between O₃, NO and NO₂ indicates crossover points between the species occur when the concentration of NOₓ (= NO + NO₂) is ~60 ppb. Under low NOₓ regime ([NOₓ] < 60 ppb), O₃ is the dominant species, while, under high NOₓ regime ([NOₓ] > 60 ppb), NO dominates. Linear regression analysis between the concentrations of Oₓ (= O₃ + NO₂) and NOₓ provides the role of local and regional contributions to Oₓ. During O₃ episodes ([O₃]hourly > 100 ppb), the values of the local and regional contributions were nearly double of those during non-episodes. Ratio analysis suggests that the major contributors of primary pollutants over BMR are mobile sources. The Air Quality Index (AQI) for BMR was predominantly good to moderate, however, unhealthy O₃ categories were observed during episode conditions in the region.

1. Introduction

Over the last three decades, Thailand’s rapid industrialization and urbanization has led to an increase in global economic prowess (World Bank, 2018). A majority of the country’s development has occurred within and around Bangkok (BKK) (13.7° N and 100.5° E), the capital city of Thailand and Bangkok Metropolitan Region (BMR). BMR is comprised of BKK and the five adjacent provinces of BKK (World Bank, 2018 and 2018a). The increase in emissions is due to accelerated growth in automotive and industrial activities. As a major metropolitan area, BMR
is dominated by mobile emissions sources, which contributes to the emissions of CO and NOx, precursors of ozone (O3) formation. The emissions from industrial activities also contributes to those emissions, and to the emissions of sulfur dioxide (SO2) and the formation of particulate matter. Since 1995, BMR has begun to experience air quality degradation and experienced exceedances in Thailand NAAQs for particulate matter (PM) and ozone (O3) (PCD, 2015) owing to strong solar radiation (peak density of direct radiation ~1,350 kWh m\(^{-2}\) yr\(^{-1}\)), high temperature (yearly average ~29 °C), and high humidity (yearly average ~64%) (Kumar et al., 2012).

The relationship between air pollution and public health in BMR has been observed in several published studies. Ruchirawat et al. (2007) reported that children who lived in BKK were exposed to high levels of carcinogenic air pollutants which might cause an elevated cancer risk. Buadong et al. (2009) reported the exposure to elevated PM and O3 during the previous day, in elderly patients (≥ 65 years), was associated with increasing the number of daily hospital visits for cardiovascular diseases. Jinsart et al. (2002, 2012) reported police personnel and drivers in BKK tended to be exposed to higher level of PM concentrations compared with the general environment.

Several studies have demonstrated the role of atmospheric processes in elevating Thailand’s O3. Long-range transport from the Asian continent has enhanced O3 concentrations in Thailand compared to the lesser O3 concentrations disbursed using long-range transports from the Indian Ocean (Pochanart et al., 2001). This regional transport, moreover, played an important role in seasonal fluctuations of O3 in this area (Zhang and Oahn, 2002). Another factor that enhanced O3 concentrations was the atmospheric chemistry of volatile organic compounds (VOCs). However, this process tended to be more important to enhance O3 concentrations in suburban areas than in urban areas (Suthawaree et al., 2012).

Therefore, the availability and analysis of multi-year measurements of such gaseous criteria pollutants in the BMR will improve our understanding of how they contribute to the air quality of this area. In this study, we analysed diurnal variations, seasonal variations and inter-annual trends of gaseous pollutants including carbon monoxide (CO), nitric oxide (NO), nitrogen dioxide (NO\(_2\)), SO\(_2\) and O\(_3\) during 2010 to 2014, in BMR. Chemical and physical processes associated with high O\(_3\) concentrations have been investigated. Since the concentrations of nitrogen oxide (NO\(_x\)) were mostly measured at the monitoring station, therefore, O\(_3\) precursors in this study is referred to NO\(_x\). The photochemical reaction for O\(_3\) was investigated during the
photostationary state. The effects of local emission and regional contributions of $O_3$ are presented. The severity of air pollution concentrations in BMR on human health are assessed by performing Air Quality Index (AQI).

2. Methodology

2.1 Study Area

Figure 1 shows a map of BMR, the location of monitoring stations in this study and major monsoon winds over this region. BMR refers to BKK and the five adjacent provinces, including Nakhon Pathom, Pathum Thani, Nonthaburi, Samut Prakan, and Samut Sakhon. These provinces are linked to BKK in terms of traffic and industrial development (Zhang and Oanh, 2002). Thailand has three official seasons—local summer (February to May), rainy (May to October) and local winter (October to February) as per the Thai Meteorological Department (TMD) (TMD, 2015). During the rainy season, this region’s weather is influenced by Southwest monsoon wind that travels from the Indian Ocean to Thailand. This marine air mass contains high moisture, resulting in the wet season in Thailand. During this season, Thailand is characterized by cloudy weather with high precipitation and high humidity. From October to April, this region is influenced by Northeast monsoon wind that travels from the north-eastern and the northern parts of Asia (China and Mongolia). This monsoon wind brings a cold and dry air mass, which leads to the dry season (local summer and local winter) in Thailand. The local winter in Thailand is characterized by cool and dry weather, while the local summer is characterized by hot (35 to 40 °C) to extremely hot weather (> 40 °C) due to strong solar radiation. During the dry season, storms may occur during the seasonal transition (TMD, 2015).

Transportation and industrial sectors are considered to be the major sources of air pollutants in the study area (Watcharavitoon et al., 2013). In 2014, ~36 million new vehicles were registered in Thailand and 29% of these cars were registered in BKK (DLT, 2015). About 56% and 28% of the registered vehicles in BKK were gasoline and diesel engines. The remaining 16% were Compressed Natural Gas (CNG) (DLT, 2017). In fact, the outskirts of BKK are populated with a variety of metal, auto parts, paper, plastic, food and chemical manufacturing facilities and power plants (DIW, 2016; 2016a; 2016b; 2016c and 2016d).
2.2 Data Collection and Data Analysis

Over the five-year period, January 1, 2010 to December 31, 2014, hourly observations from 15 Pollution Control Department (PCD) monitoring stations were analysed. The monitoring stations are categorized into three categories: BKK sites, roadside sites, and BKK suburb sites. BKK sites refer to the monitoring stations that are located within BKK’s residential, commercial, industrial and mixed areas. They are within ~50 to 100 m away from the road. Roadside sites refer to the monitoring stations that are located in BKK within 2 to 5 m from the road (Zhang and Oanh, 2002). BKK suburb sites refer to the monitoring stations that are located in the provinces adjacent to BKK (Figure 1). Quality assurance and quality control on the data set were performed by PCD prior to receiving the data. Hourly observations of the gaseous pollutants and meteorological parameters were automatically collected with auto calibration at the monitoring stations. Manual quality control was performed when unusual observations were found. External audit of the equipment and monitoring stations were done every year. Data availability and details of equipment calibrations are provided in Section I, supplement material.

Gaseous species were measured at 3 m above ground level (AGL). CO was measured using non-dispersive infrared detection (Thermo Scientific 48i). NO and NO$_2$ were measured using chemiluminescence detection (Thermo Scientific 42i). SO$_2$ was measured using ultraviolet (UV) fluorescence detection (Thermo Scientific 43i) and O$_3$ is measured by using UV absorption photometry detection (Thermo Scientific 49i). The meteorological parameters including wind speed (WS) and wind direction (WD) were measured at 10 m AGL by cup propeller and potentiometer wind vanes. Temperature (T) and relative humidity (RH) were measured at 2 m AGL by thermistor and thin film capacitor, respectively (Watchravitoon et al., 2013). All the meteorological measurements were made by Met One or equivalent method.

Data analysis, statistical analysis and plots were developed using Excel 2016. Predominant wind directions related to O$_3$ concentrations are obtained using Openair package (tool for the analysis of air pollution data) on the RStudio program (https://www.rstudio.com/).
3. Result and Discussion

3.1 Status of Pollution in BMR during 2010 to 2014

Figure 2 a) to e) show the maximum and average concentrations of gaseous pollutants, during 2010 to 2014 from the 15 monitoring stations. These concentrations are compared with the hourly NAAQs of Thailand (NAAQs of Thailand for hourly CO, NO₂, SO₂ and O₃ are 30 ppm, 170 ppb, 300 ppb and 100 ppb, respectively (PCD, 2018). Since, NO is not a criteria pollutant, only the maximum and average concentrations are presented. During the study period, the maximum concentrations of CO, NO₂ and SO₂ were mostly in their hourly standards (an exceedance of NO₂ was found at 52T monitoring station, during 2013). However, the maximum concentrations of O₃ exceeded its standard. Elevated CO, NO, and NO₂ concentrations were frequently observed at roadside sites than other sites. The average concentrations of CO, NO, and NO₂, at roadside sites, were ~1.0±0.1 ppm, ~60.5±42.7 ppb, and ~30.9±8.1 ppb, respectively. Elevated SO₂ were commonly observed at BKK suburb sites than other sites. The average concentrations of SO₂ at BKK suburb sites were ~4.0±2.3 ppb. The average concentrations of O₃ during daytime (6:00 to 18:00 LT) over BKK sites, roadside sites and BKK suburb sites were ~24.4±13.5 ppb, ~18.2±12.3 ppb and ~27.7±14.7 ppb, and those values during night-time (18:00 to 6:00 LT) were ~11.3±3.3 ppb, ~9.1±4.9 ppb and ~14.2±5.4 ppb, respectively. The 24-hour average O₃ concentrations were highest at BKK suburb sites (~21.4±3.3 ppb) and following by BKK sites (18.6±2.3 ppb) and roadside sites (13.9±8.6 ppb). Statistical analysis of the concentrations of gaseous pollutants at the three monitoring types are provided in Table I, Section B, supplement material.

The seasonal variations of the gaseous pollutants reveal that, in general, elevated concentrations were observed during dry seasons and those decreased during wet seasons (Figure II, Section C, supplement material). Inter-annual variations of the gaseous pollutants reveal that while the concentrations of CO, NO₂ and SO₂ decreased or remained constant, the concentration of O₃ tended to increase during the study period (Figure III, Section D, supplement material).

An O₃ exceedance was recorded when an hourly concentration of O₃ was greater than 100 ppb (hourly O₃ standard). Figure 2 f) to g) illustrate the number of hourly O₃ exceedances, which they are shown by locations and by seasons, respectively. The hourly O₃ exceedances at BKK
suburb sites were more frequently observed than those at the other sites. The average number of hourly \( O_3 \) exceedances was \( \sim 16 \) hours year\(^{-1} \) at BKK sites, \( \sim 9 \) hours year\(^{-1} \) at roadside sites and \( \sim 43 \) hours year\(^{-1} \) at BKK suburb sites. The hourly \( O_3 \) exceedances were commonly observed during dry season, less during the transitional period between the seasons (May), and rarely observed during wet season.

### 3.2 Diurnal Variation of the Gaseous Species

Diurnal variations of gaseous pollutant are shown in Figure 3a) to c). The diurnal variations of \( O_3 \) show a single-peak pattern (Aneja et al., 2001) with the concentrations increasing after sunrise and reached the peak \( \sim 15:00 \) local time (LT). The concentrations begin to decline in the evening and reach the minimum concentrations \( \sim 7:00 \) LT in the next morning. The concentrations of \( O_3 \) at the peaks were \( \sim 40 \) ppb at BKK sites, \( \sim 30 \) ppb at roadside sites and \( \sim 45 \) ppb at BKK suburb sites. The diurnal variations of NO show a bimodal pattern with the concentrations reach the first- and the second-peak \( \sim 7:00 \) to 9:00 LT and \( \sim 21:00 \) to 22:00 LT, respectively. The concentrations of NO at the first- and the second-peak were \( \sim 40 \) ppb and \( \sim 23 \) ppb at BKK sites, \( \sim 110 \) ppb and \( \sim 73 \) ppb at roadside sites, and \( \sim 30 \) ppb and \( \sim 13 \) ppb at BKK suburb sites. The concentrations of \( NO_2 \) at the first- and the second-peak were \( \sim 23 \) ppb and \( \sim 28 \) ppb at BKK sites, \( \sim 33 \) ppb and \( \sim 37 \) ppb at roadside sites, and \( \sim 20 \) ppb and \( \sim 22 \) ppb at BKK suburb sites. Even the diurnal variations of \( NO_x \) show a bimodal pattern, at roadside sites, the pattern was flatter than at other sites. The flatter pattern of \( NO_x \) at roadside sites reveals that this monitoring station type was affected by high concentration of \( NO_x \) all day. The diurnal variations of CO show a bimodal pattern with the first- and the second-peak occurred \( \sim 8:00 \) LT and 21:00 LT, respectively. The concentrations of CO at the first- and the second-peak were \( \sim 1 \) ppm (both peaks) at BKK sites, \( \sim 2 \) and \( \sim 1.5 \) ppm at roadside sites, and \( \sim 1 \) ppm (both peaks) at BKK suburb sites. The first peak of the diurnal variations of NO, \( NO_2 \), and CO correspond with morning rush hour in BKK (7:00 to 9:00 LT). The second peak of those occurred \( \sim 3 \) to 5 hours after the evening traffic rush hour (16:00 to 18:00 LT) (Leong et al., 2002), due to a combination of pollutants emissions and collapse of the planetary boundary layer (weak turbulence and diffusion) during this time. The diurnal variations of \( SO_2 \) show a bimodal pattern with the first- and the second-peak of \( SO_2 \) occurred \( \sim 8:00 \) LT and 21:00 LT, respectively. The concentrations of \( SO_2 \) at the first- and the second-peak were \( \sim 4 \) ppb and \( \sim 3 \) ppb at BKK sites and roadside sites, and \( \sim 6 \) ppb and \( \sim 3 \) ppb at BKK suburb sites.
At the roadside sites, the peaks are more obvious than the other sites. The result indicates that at this monitoring station type, SO$_2$ is primarily influenced by emissions from vehicle exhaust using high sulfur content fuel (Henschel et al. 2013). It is noteworthy that BKK has a large diesel engine fleet (an estimated 25% of registered vehicles) (DLT, 2015). The diesel fuel contains ~0.035% wt Sulphur (DOEB, 2017). Season wise of the diurnal variations are provided in Figure IV, Section E, supplement material.

Figure 4 a) to c) shows diurnal variations of rate of change of O$_3$ concentration ($\Delta$[O$_3$/dt]) during dry seasons (local summer and local winter) and wet seasons at the three monitoring station types (the data has been averaged for each monitoring station type to capture the rate of change of O$_3$ concentration characteristics). The diurnal variations of $\Delta$[O$_3$/dt] is a combination of O$_3$ chemistry and meteorology. In general, $\Delta$[O$_3$/dt] during wet season were lower than those during dry season. However, during local winter, the rates of change O$_3$ concentration were the highest. The $\Delta$[O$_3$/dt] at the three monitoring station types, during 10:00 to 11:00 LT, were 4.5 to 7.0 ppb hr$^{-1}$ during wet seasons, 6.7 to 7.5 ppb hr$^{-1}$ during local summers, and 5.7 to 9.2 ppb hr$^{-1}$ during local winters. The $\Delta$[O$_3$/dt] became negative during 14:00 to 15:00 LT. As expected, the rate of change of O$_3$ concentration was nearly constant during nighttime. Rapid changes in the mixing height and solar insolation during morning increases $\Delta$[O$_3$/dt]. After sunset, the formation of O$_3$ is inhibited and the planetary boundary layer becomes more stable resulting in O$_3$ reduction through chemical reactions (for example, the oxidation of O$_3$ by NO$_x$) and physical processes (for example, dry deposition to the earth surface) (Naja and Lal, 2002).

### 3.3 Photochemical Reaction and Interconversion between O$_3$, NO and NO$_2$

The primary precursors for tropospheric O$_3$, in the urban environment, are NO$_x$ and non-methane volatile organic compounds (VOCs), methane or CO (The Royal Society, 2008; Monks et al., 2009; Cooper et al., 2014). While NO$_x$ was measured continuously at all the monitoring sites, VOCs were measured periodically only at one monitoring station limiting its usefulness as part of this study. In this study, the photostationary state (PSS) is applied through the chemical reactions of O$_3$ formation during 10:00 to 16:00 LT. This time window is chosen due to the fully developed planetary boundary layer with well-mixed condition (Pochanart et al., 2001) to avoid
accumulation of air pollutants by surface inversion. Analysis and calculation are performed only during dry season to eliminate effects of the removal process by wet deposition.

The relationship among NO, NO\(_2\) and O\(_3\) under PSS is presented by Eq. (1) (Seinfeld and Pandis, 1998).

\[
[O_3]_{PSS} = \frac{j_1[NO_2]}{k_3[NO]} \tag{Eq. (1)}
\]

Where \([O_3]_{PSS}\) is the concentration of O\(_3\), at PSS, \(j_1\) and \(k_3\) are reaction rate coefficient of photochemical reaction of NO\(_2\) and reaction rate coefficient of chemical reaction between NO and O\(_3\), respectively.

The values for \(k_3\) (ppm\(^{-1}\) min\(^{-1}\)) is calculated by Eq. (2) (Seinfeld and Pandis, 1998; Tiwari et al., 2015).

\[
k_3 = 3.23 \times 10^1 \exp[-1430/T] \tag{Eq. (2)}
\]

During dry seasons, the values of \(j_1\) ranged from 0.12 to 1.22 min\(^{-1}\), and the average of those at BKK sites, roadside sites and BKK suburb sites were 0.74±0.2, 0.64±0.3 and 0.55±0.3 min\(^{-1}\), respectively. The rate coefficients are calculated using the NCAR TUV model, during 2010 the dry season, for 10:00 LT to 16:00 LT, at the latitude and longitude of 13.76 °N and 100.50 °E. The average \(j_1\) value calculated from the NCAR TUV model is 0.021±0.0024 s\(^{-1}\), which is similar to the calculated \(j_1\) values from Eq. (1) (\(j_1\) ranges from 0.008 to 0.013 s\(^{-1}\)). The values of \(j_1\) from this study are similar to those values at an urban background site in Delhi, India (values of \(j_1\) ranged from 0.4 to 1.8 min\(^{-1}\) and the average was 0.8 min\(^{-1}\)) (Tiwari et al., 2015) and those values collected during a November daytime in the UK (values of \(j_1\) was ~0.14 min\(^{-1}\)) (Clapp and Jenkin, 2001).

The values of \(k_3\), during dry seasons, ranged from 28.3 to 30.9 ppm\(^{-1}\) min\(^{-1}\), and the average of those at BKK sites, roadside sites and BKK suburb sites were 29.8±0.7, 29.7 and 29.8±0.7 ppm\(^{-1}\) min\(^{-1}\), respectively. The ratio of \([NO_2]\) and \([NO]\) was ~1.9. The statistical analysis of \(j_1\) (min\(^{-1}\) and s\(^{-1}\)) and \(k_3\) (ppm\(^{-1}\) min\(^{-1}\) and cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) at the three monitoring station types using Eq. (1), and the average \(j_1\) calculated from the NCAR TUV model are provided in Table II, Section F, supplement material.

Figure 5 a) to c) shows the relationships between NO, NO\(_2\) and O\(_3\), their crossover points, and concentration distributions. The crossover point among species occurs when the concentration
of NO$_x$ is ~60 ppb. At this point, two regimes are identified, including low NO$_x$ regime and high NO$_x$ regime. Under the low NO$_x$ regime ([NO$_x$] < 60 ppb), O$_3$ is the dominant species among the others and NO$_2$ concentrations are higher than NO for NO$_x$ species. Conversely, under the high NO$_x$ regime ([NO$_x$] > 60 ppb), NO and NO$_2$ increase and the concentrations of O$_3$ rapidly decrease. Under the high NO$_x$ regime, the declination of O$_3$ trend-lines may describe O$_3$ removal process through the titration of O$_3$ by NO.

3.4 Local and Regional Contribution to O$_x$

The O$_x$ concentration is the summation of O$_3$ and NO$_2$ concentration. Under the PSS condition, concentration of NO, NO$_2$ and O$_3$ approach an equilibrium and the concentration of O$_x$ may be considered constant (Keuken et al., 2009). Since the conversion between O$_3$ and NO$_2$ in the urban and suburban atmosphere is rapid, the use of O$_x$ to represent production of oxidants is more appropriate than only using O$_3$ (Lu et al, 2010). The local or NO$_x$-dependent contribution refers to O$_x$ concentration that is influenced by concentration of the local pollutants. The regional contribution or NO$_x$-independent refers to the background concentration of O$_x$ that is not influenced by changes of the local pollutants (Clapp and Jenkin, 2001; Tiwari et al. 2015).

Figure 6 a) to c) shows the local and regional contributions of O$_x$ at the three monitoring station types. The effects of the local and regional contributions to O$_x$ concentration are analysed by plotting O$_x$ concentrations against NO$_x$ concentrations and fitting the plot with a linear regression ($y = mx + c$). The concentration of NO$_x$ and O$_x$ are referred by x and y, respectively. The slope of the linear regression (m) implies the local contribution and the intercept with the y-axis (c) implies the regional (background) contribution (Aneja et al., 2000; Clapp and Jerkin, 2001; Notario et al., 2012). Table 1 shows the comparison between fitted linear regressions from this study with fitted linear regression lines from other studies. The average background O$_x$ concentrations over BMR during non-episodes ([O$_3$]$_{hourly}$ < 100 ppb) and episodes ([O$_3$]$_{hourly}$ > 100 ppb) were ~48 ppb and ~95 ppb, respectively. The local and regional contributions during the episode days, in general, were about double of those during the non-episode days. The results reveal that elevated O$_3$ concentrations during the episode days are influenced by both the local and regional contributions of O$_x$. It is noteworthy that the pattern of the local and regional contributions at roadside sites during non-episode period is composed of two NO$_x$ concentration regimes. The
low NO\textsubscript{x} regime (NO\textsubscript{x} < 60 ppb) resembles the local and regional contributions during non-episode over BKK suburb sites. The high NO\textsubscript{x} regime (NO\textsubscript{x} > 60 ppb) may represent typical characteristic of air quality near roads.

The local contributions from the fitted linear regressions are compared with the local contribution that is calculated from delta O\textsubscript{3} method. A delta O\textsubscript{3} (\Delta O\textsubscript{3}) analysis was performed to reflect on the intensity of O\textsubscript{3} production in BMR area (Lindsay and Chameides, 1988). Lindsay et al. (1989) analysed high-O\textsubscript{3} events in Atlanta, GA, and showed that rural background O\textsubscript{3} during high O\textsubscript{3} concentrations ([O\textsubscript{3}] > 80 ppb) in Atlanta Metropolitan Area were higher than its average and the concentration of O\textsubscript{3} increased from ~15 to 20 ppb when the air mass travelled across the city. This enhanced the total O\textsubscript{3} concentration to 80 to 85 ppb. In our study, during the different in the concentrations of O\textsubscript{3} at the upwind and downwind monitoring stations (20T and 27T monitoring station) are averaged. The conditions to calculate \Delta O\textsubscript{3} in this study are 1) high O\textsubscript{3} concentrations ([O\textsubscript{3}] > 80 ppb) were observed at least one of the two monitoring stations 2) the calculation is performed 10:00 to 16:00 LT, during dry season, to avoid accumulation of air pollutants by surface inversion and effects of the removal process by wet deposition 3) National Oceanic and Atmospheric Administration (NOAA) HYSPLIT model backward trajectories revealed N-NE, S-SW wind directions (Figure 7). Even the O\textsubscript{3} concentrations at the downwind monitoring stations are expected to be greater than the O\textsubscript{3} concentrations at the upwind monitoring stations, a negative \Delta O\textsubscript{3} may be found. The negative \Delta O\textsubscript{3} suggests deposition of O\textsubscript{3} and/or O\textsubscript{3} was consumed as it passes over the city and/or there may have been a wind reversal so that air already polluted by the metropolitan area was brought back in to the city (Lindsay et al., 1989). The \Delta O\textsubscript{3} in BMR ranged from -53 to 86 ppb (average ~10.4 ppb.) and ranged from -66 to 96 ppb (average ~9.4 ppb.) when the predominant wind direction advecting into the city were from NE and SW, respectively. Thus, we find that there was ~10 ppb enhancement of the O\textsubscript{3} concentration during the air pollution high O\textsubscript{3} concentration in BMR ([O\textsubscript{3}] > 80 ppb), which corroborates local O\textsubscript{3} production analysis based on linear regression.
3.5 Correlation of Air Pollutants

3.5.1 Local Sources Analysis

Characteristic of emission sources are often determined by the ratios between CO and NO\textsubscript{x} (CO/NO\textsubscript{x}) and SO\textsubscript{2} and NO\textsubscript{x} (SO\textsubscript{2}/NO\textsubscript{x}). In general, the major sources of NO\textsubscript{x} are point sources and mobile sources. However, NO\textsubscript{x} from point sources is more likely correlated with SO\textsubscript{2}. NO\textsubscript{x} from mobile sources is more likely correlated with CO (Parrish et al., 1991). Therefore, the characteristics of mobile source are high CO/NO\textsubscript{x} ratios and low SO\textsubscript{2}/NO\textsubscript{x} ratios. In contrast to mobile sources, the characteristic of point sources are low CO/NO\textsubscript{x} ratios and high SO\textsubscript{2}/NO\textsubscript{x} ratios (Parrish et al., 1991; Rasheed et al., 2014).

Table 2 shows the comparison between the CO/NO\textsubscript{x} and SO\textsubscript{2}/NO\textsubscript{x} ratios from this study and when compared with other studies. The ratio of CO/NO\textsubscript{x} is 19.8 and the ratio of SO\textsubscript{2}/NO\textsubscript{x} is 0.1 over BMR. This suggests that the major contributors of primary pollutants over the BMR are mobile sources. However, this region may be influenced by manufacturing facilities’ point sources (SO\textsubscript{2} contributor) on the outskirts of the BKK. These point sources will impact the concentrations of SO\textsubscript{2}, NO\textsubscript{x} and CO. Correlations among species are provided in Table II, Section G, supplement material.

3.5.2 Effects of Pollutant Transport

In general, O\textsubscript{3} has a short lifetime in polluted urban atmosphere (approximately hours). However, O\textsubscript{3} has a longer lifetime of several weeks in the free troposphere. This occurrence may allow O\textsubscript{3} to be transported over continental scales (Stevenson et al., 2006; Young et al., 2013; Monks et al., 2015). Figure 8 shows O\textsubscript{3} concentrations, during episodes and non-episodes, with predominant wind directions and wind speeds. The results show that O\textsubscript{3} exceedances are associated with low wind speed and predominant wind directions i.e. origins of the air masses. In general, elevated O\textsubscript{3} concentrations were observed with wind speed lower than 4 m\textsuperscript{s}\textsuperscript{-1} with northerly winds (22T station), southerly winds (3T, 10T, 19T, 20T and 61T stations) and westerly winds (52T station). It is noteworthy that the southerly winds, generally, bring cleaner marine air mass to the land. However, under a stagnant condition (i.e. low wind speed), elevated O\textsubscript{3} concentrations were observed during southerly winds (Sahu et al., 2013; 2013a).
3.6 Air Quality Index for O₃ Management

Air Quality Index (AQI) for air pollutants, in the US, is categorized into six categories (good, moderate, unhealthy for sensitive groups, unhealthy, very unhealthy, and hazardous). These categories are nonlinear and relate to human health (US.EPA, 2017, 2017a, 2017b). In Thailand, the NAAQs for the air pollutant species is pegged at an AQI value of 100. In this study, the severity of O₃ concentrations in BMR is evaluated by AQI for O₃. Table 3 provides the ambient air quality over BMR during 2010 to 2014 based on the AQI of O₃. Based on the AQI for O₃, during the study period, the majority of air quality over BMR was in the good AQI category (~97 %), followed by the moderate air quality category (~2.3%). However, unhealthy for sensitive group (~0.7 %), unhealthy (~0.3%) and very unhealthy (~0.04%) O₃ air quality categories were observed. Generally, BKK suburb sites have higher number of hours that were found in the unhealthy for sensitive group, unhealthy and very unhealthy categories than BKK and roadside sites. The average number of hours that were found in unhealthy for sensitive group, unhealthy and very unhealthy categories over BKK suburb sites were 425.8, 146.7 and 28.7 hours. The calculation of the AQI for O₃ can be found in Section H, supplement material.

This study provides measurements and analysis for the gaseous criteria pollutants. However, in order to provide a well-established air quality management policy, the integration of multidisciplinary analysis is needed. This will include scientific, socioeconomic, and policy analysis (Aneja et al, 2001). The results from this study revealed evidence of violations for O₃ for air quality. This resulted in adverse health effects, human welfare, economics, and environment over BMR. Ratio analysis suggests that the first priority should be controlling pollution emissions from local sources that come primarily from mobile sources. The complexity between O₃ and its precursors and the effects of pollution transport shows that decreasing only NOₓ emissions and/or local emissions may not be an effective policy to reduce O₃ since regional air pollution transport (i.e. ozone and its precursors contribute to O₃ exceedances). To identify the proportional contribution between local and regional sources of O₃ concentrations during selected O₃ episode days, atmospheric modeling is needed to quantify various processes that contribute to the ambient concentration at specific locations. This scientific analysis provides a frame work for the process of establishing an air quality policy while developing socioeconomic impacts.
4. Conclusion

Among measured gaseous criteria pollutants, $O_3$ is the only specie whose concentrations frequently exceed the NAAQs of Thailand. The $O_3$ exceedances occur during the dry season (local summer and local winter) and most frequently occur over BKK sites and BKK suburb sites than roadside sites. On average, the number of hourly $O_3$ exceedances at BKK sites, roadside sites and BKK suburb sites were $\sim$16 hours year$^{-1}$, $\sim$9 hours year$^{-1}$ and $\sim$43 hours year$^{-1}$, respectively. The lower number of $O_3$ exceedances at roadside sites demonstrates the effects of the titration of $O_3$ by NO, due to, high concentrations of NO that were generally observed at this monitoring type (average $[\text{NO}]_{\text{hourly}} = \sim 166.0 \pm 19.8$ ppb). Under photostationary state assumption, during dry season, the values of reaction rate coefficient of photochemical reaction of NO$_2$ ($j_j$) and reaction rate coefficient of chemical reaction between NO and $O_3$ ($k_3$) range from 0.12 to 1.22 min$^{-1}$ and range from 28.3 to 30.9 ppm$^{-1}$ min$^{-1}$, respectively. NO$_x$ values of $\sim$ 60 ppb, marks the threshold for the interconversion between $O_3$, NO and NO$_2$. Under the low NO$_x$ regime ($[\text{NO}_x] < 60$ ppb), $O_3$ is the dominant species. On the other hand, under the high NO$_x$ regime ($[\text{NO}_x] > 60$ ppb), the concentrations of $O_3$ rapidly decrease. The decrease of $O_3$ under the high NO$_x$ regime describes the important role of NO in destroying $O_3$ in the atmosphere in polluted environments. The local and regional contributions of $O_x$ concentrations, under stagnant condition (wind speed $< 4$ m s$^{-1}$) and origin of air masses containing $O_3$ and its precursors associate with elevated $O_3$ concentration in this area. During $O_3$ episodes, the values of the local and regional contributions were about double of those during non-episodes. Air Quality Index for $O_3$ reveals evidence of violations for air quality standards, in BMR, resulting in potential adverse health effects. To achieve $O_3$ reduction, control strategies may be needed. Emissions from mobile sources may be the first priority to manage $O_3$, since BMR is more likely affected by mobile sources than point sources ($\text{CO/NO}_x = 19.8$ and $\text{SO}_2/\text{NO}_x = 0.1$). Due to the highly nonlinear physical and chemical processes governing the atmosphere, control strategies need to be evaluated in a more comprehensive approach. Air quality modelling of pollution episodes in the BMR would be an appropriate approach to accurately quantify various atmospheric processes contributing to high $O_3$ concentrations in BMR.
Data Availability

Hourly observations in this study were provided by Pollution Control Department (PCD), Thailand.
Address: 92 Phahonyothin Rd, Khwaeng Samsen Nai, Khet Phaya Thai, Krung Thep Maha Nakhon 10400, Thailand.
Phone: +66 2 298 2000
Website: http://www.pcd.go.th/

Competing Interest

The authors declare that they have no conflict of interest.

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DLT: Statistic of registered vehicle in Bangkok, categorized by fuel types, Department of land transport, Thailand,
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Figures:

**Fig. 1:** Map of BMR, the location of monitoring stations and two major monsoons winds (from NOAA HYSPLIT back trajectory model). Three monitoring station types, including BKK sites, roadside sites and BKK suburb sites are shown in light blue dots, purple dots and blue dots, respectively. (Note: * the station has been closed since 1 October 2013).
Fig 2: Maximum (vertical bars) and average (solid line) concentrations of a) CO, b) SO$_2$, c) NO$_2$ d) O$_3$ and e) NO from the 15 monitoring stations, during 2010 to 2014, are compared with the hourly NAAQs (dotted line) of Thailand (except NO which is not a criteria pollutant). The number of hourly O$_3$ exceedances is shown by f) locations and g) seasons.
Fig 3: Diurnal variations of gaseous species. The plots provide the average concentrations of O$_3$, NO and NO$_2$ in ppb, the average concentrations of CO in ppm and the average concentrations of SO$_2$ in ppb at a) BKK site; b) roadside sites; and c) BKK suburb sites. Vertical bars provide ±1 standard deviations of the species concentrations.
Fig. 4: Diurnal variations of rate of change of O₃ concentration ($\Delta$[O₃]/dt) during a) local summers b) wet seasons and c) local winters.
Fig. 5: Relationships and crossover points of NO, NO\textsubscript{2} and O\textsubscript{3} at a) BKK sites b) roadside sites and c) BKK suburb sites; and concentration distributions of those species at d) BKK sites e) roadside sites and f) BKK suburb sites.
Fig. 6: Effects of local and regional contributions on $O_x$ during non-episode and episode days at a) BKK sites, b) roadside sites and c) BKK suburb sites.
Fig. 7: Backward trajectories from HYSPLIT model reveal a) NE wind direction (Jan 13, 2010) and b) SW wind direction (Jan 1, 2010)
Fig. 8: Relationship between the concentrations of O$_3$, wind speeds and wind directions during a) O$_3$ episodes ([O$_3$]$_{hourly}$ > 100 ppb) and b) during non O$_3$ episodes ([O$_3$]$_{hourly}$ ≤ 100 ppb), over BMR during 2010 to 2014.
**Tables:**

**Table 1:** The comparison of fitted linear regression lines from this study, including at BKK sites, roadside sites, and BKK suburb sites with fitted linear regression lines from other studies.

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<tr>
<th></th>
<th>Non-Episode</th>
<th>Episode</th>
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<tr>
<td><strong>This study</strong></td>
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<tr>
<td>- BKK sites</td>
<td>$[O_3] = 0.33[NO_x]+44.39$</td>
<td>$[O_3] = 0.48[NO_x]+91.10$</td>
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<td>- Roadside sites</td>
<td>$[O_3] = 0.13[NO_x]+53.89$</td>
<td>$[O_3] = 0.29[NO_x]+104.45$</td>
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<tr>
<td>- BKK suburb sites</td>
<td>$[O_3] = 0.31[NO_x]+47.0$</td>
<td>$[O_3] = 0.68[NO_x]+82.89$</td>
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<td>UK*</td>
<td>$[O_3] = 0.097[NO_x]+38.2$</td>
<td>$[O_3] = 0.112[NO_x]+55.5$</td>
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<td>Buenos Aires, Argentina**</td>
<td>$[O_3] = 0.099[NO_x]+22.0$</td>
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<tr>
<td>Delhi, India***</td>
<td>$[O_3] = 0.54[NO_x]+28.89$</td>
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Note: *Clapp and Jenkin (2001), **Mazzeo et al. (2005), ***Tiwari et al. (2015)
Table 2: The comparison of CO/NO\textsubscript{x} and SO\textsubscript{2}/NO\textsubscript{x} ratios from this study with other studies (modify from Rasheed et al., 2014).

<table>
<thead>
<tr>
<th>Region</th>
<th>Source</th>
<th>CO/NO\textsubscript{x}</th>
<th>SO\textsubscript{2}/NO\textsubscript{x}</th>
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<td>18.25</td>
<td>0.09</td>
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<tr>
<td>- Roadside sites</td>
<td></td>
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<td>0.11</td>
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<td>- BKK suburb sites</td>
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<td>1.7</td>
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<td>Point</td>
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* Fernandez-Jiménez et al., 2003  
** Coppalle et al., 2001  
*** Mallik and Lal, 2014
Table 3: Number of hours that were found in different AQI categories of O₃ over the BMR during 2010 to 2014

<table>
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<th>AQI</th>
<th>Hour 3T</th>
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<th>10T</th>
<th>11T</th>
<th>12T</th>
<th>15T</th>
<th>61T</th>
<th>52T</th>
<th>54T</th>
<th>13T</th>
<th>14T</th>
<th>19T</th>
<th>20T</th>
<th>22T</th>
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<td>32021</td>
<td>27959</td>
<td>40715</td>
<td>26606</td>
<td>33628</td>
<td>26442</td>
<td>32665</td>
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<td>Moderate</td>
<td>310</td>
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<td>556</td>
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