Assessment of Gaseous Criteria Pollutants in Bangkok Metropolitan Region, Thailand

Pornpan Uttamang[1], Viney P. Aneja[1], Adel F. Hanna[1, 2]
[1]Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC, 27695, USA
[2]Institute for the Environment, University of North Carolina at Chapel Hill, Chapel Hill, NC, 27517, USA

Correspondence to: Pornpan Uttamang (puttama@ncsu.edu)

Abstract. Analysis of gaseous criteria pollutants in Bangkok Metropolitan Region (BMR), Thailand, during 2010 to 2014 reveals that while the hourly concentrations of CO, SO_2 and NO_2 were mostly within the National Ambient Air Quality Standards (NAAQs) of Thailand; however, the hourly concentrations of O_3 frequently exceeded the standard. The results reveal that the problem of high O_3 concentration continuously persisted in this area. The O_3 photolytic rate constant (j_1) for BMR calculated based on assuming photostationary state (ranged from 0.008 to 0.013 s^{-1}) which is similar to the calculated j_1 using the NCAR TUV model (0.021±0.0024 s^{-1}). Interconversion between O_3, NO and NO_2 indicates crossover points between the species occur when the concentration of NO_x (= NO + NO_2) is ~60 ppb. Under low NO_x regime ([NO_x] < 60 ppb), O_3 is the dominant species, while, under high NO_x regime ([NO_x] > 60 ppb), NO dominates. Linear regression analysis between the concentrations of O_x (= O_3 + NO_2) and NO_x provides the role of local and regional contributions to O_x. During O_3 episodes ($[O_3]_{hourly}$ > 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 O_3 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 NO_x, precursors of ozone (O_3) formation. The emissions from industrial activities also contributes to those emissions, and to the emissions of sulfur dioxide (SO_2) 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 (O_3) (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 O_3 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 O_3. Long-range transport from the Asian continent has enhanced O_3 concentrations in Thailand compared to the lesser O_3 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 O_3 in this area (Zhang and Oahn, 2002). Another factor that enhanced O_3 concentrations was the atmospheric chemistry of volatile organic compounds (VOCs).However, this process tended to be more important to enhance O_3 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_x 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 ℃) to extremely hot weather (> 40 ℃) 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 (Fig. 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 Fig. S1, 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, NO_2, SO_2 and O_3 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, NO_2 and SO_2 were mostly in their hourly standards (an exceedance of NO_2 was found at 52T monitoring station, during 2013). However, the maximum concentrations of O_3 exceeded its standard. Elevated CO, NO, and NO_2 concentrations were frequently observed at roadside sites than other sites. The average concentrations of CO, NO, and NO_2, at roadside sites, were ~1.0±0.1 ppm, ~60.5±42.7 ppb, and ~30.9±8.1 ppb, respectively. Elevated SO_2 were commonly observed at BKK suburb sites than other sites. The average concentrations of SO_2 at BKK suburb sites were ~4.0±2.3 ppb. The average concentrations of O_3 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 O_3 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 S1, 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 (Fig. S2, Section C, supplement material). Inter-annual variations of the gaseous pollutants reveal that while the concentrations of CO, NO_2 and SO_2 decreased or remained constant, the concentration of O_3 tended to increase during the study period (Fig. S3, Section D, supplement material).

An O_3 exceedance was recorded when an hourly concentration of O_3 was greater than 100 ppb (hourly O_3 standard). Figure 2 f) to g) illustrate the number of hourly O_3 exceedances, which they are shown by locations and by seasons, respectively. The hourly O_3 exceedances at BKK

suburb sites were more frequently observed than those at the other sites. The average number of hourly O_3 exceedances was ~16 hours year^{-1} at BKK sites, ~9 hours year^{-1} at roadside sites and ~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 Fig. 3 a) 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 ~15:00 local time (LT). The concentrations begin to decline in the evening and reach the minimum concentrations ~7:00 LT in the next morning. The concentrations of O_3 at the peaks were ~40 ppb at BKK sites, ~30 ppb at roadside sites and ~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 ~7:00 to 9:00 LT and ~21:00 to 22:00 LT, respectively. The concentrations of NO at the first- and the second-peak were ~40 ppb and ~23 ppb at BKK sites, ~110 ppb and ~73 ppb at roadside sites, and ~30 ppb and ~13 ppb at BKK suburb sites. The concentrations of NO_2 at the first- and the second-peak were ~23 ppb and ~28 ppb at BKK sites, ~33 ppb and ~37 ppb at roadside sites, and ~20 ppb and ~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 ~8:00 LT and 21:00 LT, respectively. The concentrations of CO at the first- and the second-peak were ~1 ppm (both peaks) at BKK sites, ~2 and ~1.5 ppm at roadside sites, and ~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 ~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 ~8:00 LT and 21:00 LT, respectively. The concentrations of SO_2 at the first- and the second-peak were ~4 ppb and ~3 ppb at BKK sites and roadside sites, and ~6 ppb and ~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 Fig. S4, 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 Equation (1) (Seinfeld and Pandis, 1998).

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

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 Equation (2) (Seinfeld and Pandis, 1998; Tiwari et al., 2015).

$$k_3 = 3.23\times10^3 \exp[-1430/T] \quad \text{Eq. (2)}$$

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 Equation (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 Equation (1), and the average j_1 calculated from the NCAR TUV model are provided in Table S2, 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_x regime (NO_x < 60 ppb) resembles the local and regional contributions during non-episode over BKK suburb sites. The high NO_x regime (NO_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_3 method. A delta O_3 (ΔO_3) analysis was performed to reflect on the intensity of O_3 production in BMR area (Lindsay and Chameides, 1988). Lindsay et al. (1989) analysed high-O_3 events in Atlanta, GA, and showed that rural background O_3 during high O_3 concentrations ([O_3] > 80 ppb) in Atlanta Metropolitan Area were higher than its average and the concentration of O_3 increased from ~15 to 20 ppb when the air mass travelled across the city. This enhanced the total O_3 concentration to 80 to 85 ppb. In our study, during the different in the concentrations of O_3 at the upwind and downwind monitoring stations (20T and 27T monitoring station) are averaged. The conditions to calculate ΔO_3 in this study are 1) high O_3 concentrations ([O_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 (Fig. 7). Even the O_3 concentrations at the downwind monitoring stations are expected to be greater than the O_3 concentrations at the upwind monitoring stations, a negative ΔO_3 may be found. The negative ΔO_3 suggests deposition of O_3 and/or O_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 ΔO_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_3 concentration during the air pollution high O_3 concentration in BMR ([O_3] > 80 ppb), which corroborates local O_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_x (CO/NO_x) and SO_2 and NO_x (SO_2/NO_x). In general, the major sources of NO_x are point sources and mobile sources. However, NO_x from point sources is more likely correlated with SO_2. NO_x from mobile sources is more likely correlated with CO (Parrish et al., 1991). Therefore, the characteristics of mobile source are high CO/NO_x ratios and low SO_2/NO_x ratios. In contrast to mobile sources, the characteristic of point sources are low CO/NO_x ratios and high SO_2/NO_x ratios (Parrish et al., 1991; Rasheed et al., 2014).

Table 2 shows the comparison between the CO/NO_x and SO_2/NO_x ratios from this study and when compared with other studies. The ratio of CO/NO_x is 19.8 and the ratio of SO_2/NO_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_2 contributor) on the outskirts of the BKK. These point sources will impact the concentrations of SO_2, NO_x and CO. Correlations among species are provided in Table S3, Section G, supplement material.

3.5.2 Effects of Pollutant Transport

In general, O_3 has a short lifetime in polluted urban atmosphere (approximately hours). However, O_3 has a longer lifetime of several weeks in the free troposphere. This occurrence may allow O_3 to be transported over continental scales (Stevenson et al., 2006; Young et al., 2013; Monks et al., 2015). Figure 8 shows O_3 concentrations, during episodes and non-episodes, with predominant wind directions and wind speeds. The results show that O_3 exceedances are associated with low wind speed and predominant wind directions i.e. origins of the air masses. In general, elevated O_3 concentrations were observed with wind speed lower than 4 ms^{-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_3 concentrations were observed during southerly winds (Sahu et al., 2013; 2013a).

3.6 Air Quality Index for O_3 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 O_3 concentrations in BMR is evaluated by AQI for O_3. Table 3 provides the ambient air quality over BMR during 2010 to 2014 based on the AQI of O_3. Based on the AQI for O_3, 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%) O_3 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 O_3 can be found in Fig. S5 and Fig S6, 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 O_3 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 O_3 and its precursors and the effects of pollution transport shows that decreasing only NO_x emissions and/or local emissions may not be an effective policy to reduce O_3 since regional air pollution transport (i.e. ozone and its precursors contribute to O_3 exceedances). To identify the proportional contribution between local and regional sources of O_3 concentrations during selected O_3 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 ~16 hours $year^{-1}$, ~9 hours $year^{-1}$ and ~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 $[NO]_{hourly}$ = ~166.0±19.8 ppb). Under photostationary state assumption, during dry season, the values of reaction rate coefficient of photochemical reaction of NO_2 (j_1) 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 ~ 60 ppb, marks the threshold for the interconversion between O_3, NO and NO_2. Under the low NO_x regime ($[NO_x]$ < 60 ppb), O_3 is the dominant species. On the other hand, under the high NO_x regime ($[NO_x]$> 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 (CO/NO_x = 19.8 and SO_2/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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Figures:

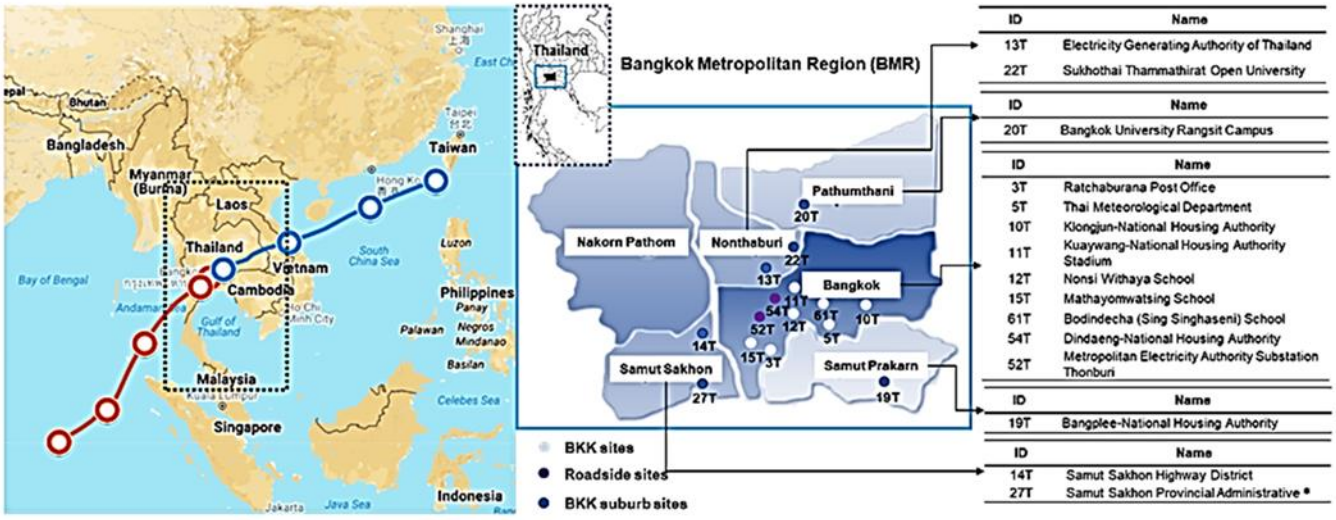
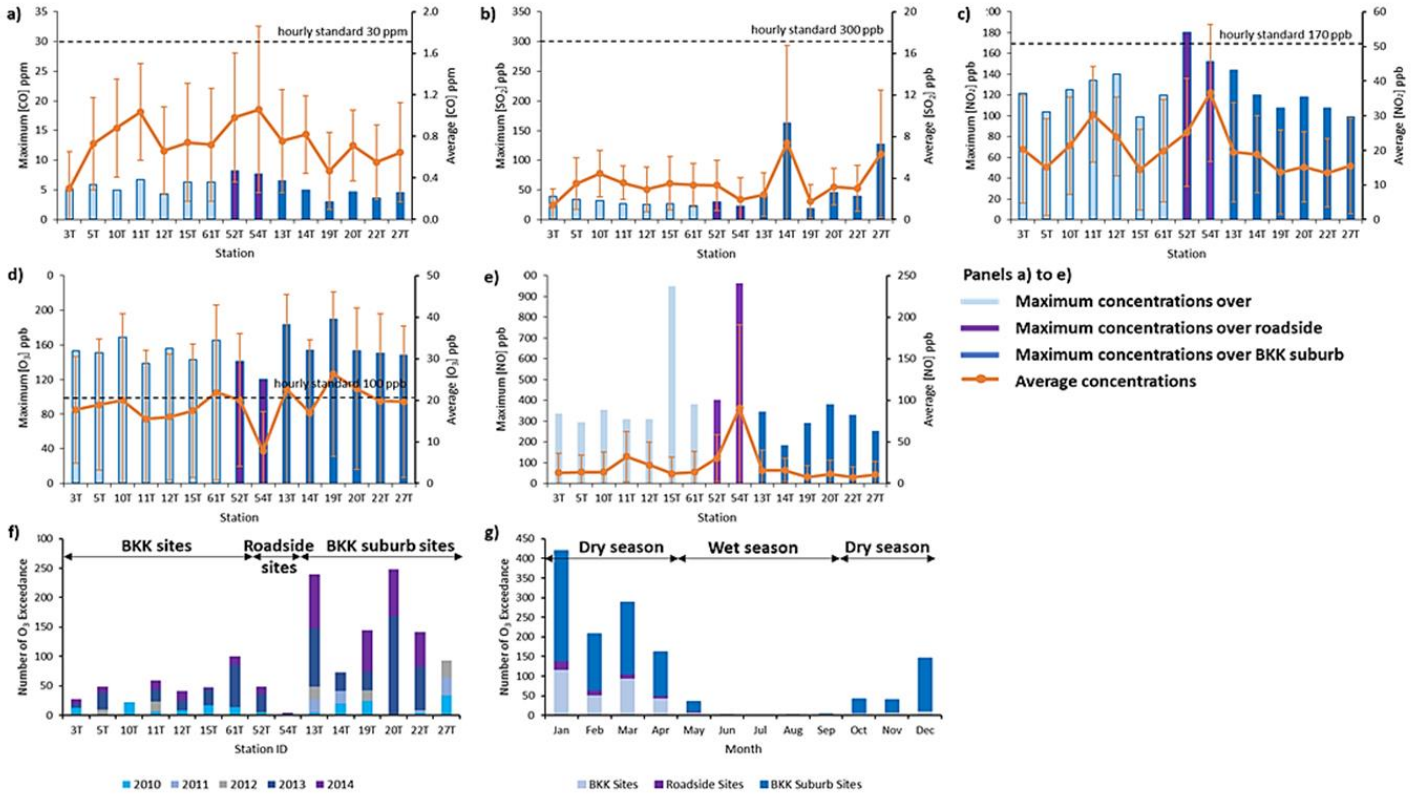


Figure 1: Map of BMR, the location of monitoring stations and two major monsoons winds (from NOAA HYSPLIT back trajectory model). Three monitoring station types, including BKK sites, roadside sites and BKK suburb sites are shown in light blue dots, purple dots and blue dots, respectively. (Note: * the station has been closed since 1 October 2013).



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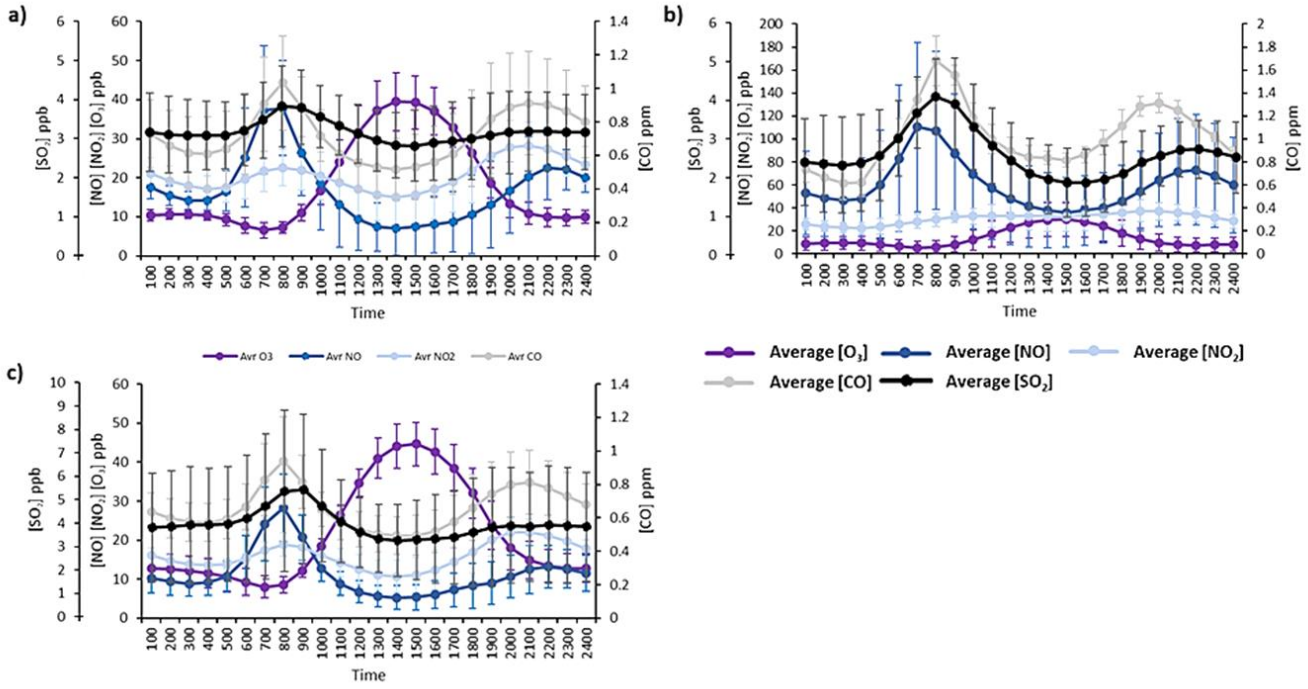
546 **Figure 2:** Maximum (vertical bars) and average (solid line) concentrations of a) CO, b) SO_2, c) NO_2 d) O_3 and e) NO from the 15
547 monitoring stations, during 2010 to 2014, are compared with the hourly NAAQs (dotted line) of Thailand (except NO which is not
548 a criteria pollutant). The number of hourly O_3 exceedances is shown by f) locations and g) seasons.



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550 **Figure 3:** Diurnal variations of gaseous species. The plots provide the average concentrations of O_3, NO and NO_2 in ppb, the
551 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
552 suburb sites. Vertical bars provide ±1 standard deviations of the species concentrations.

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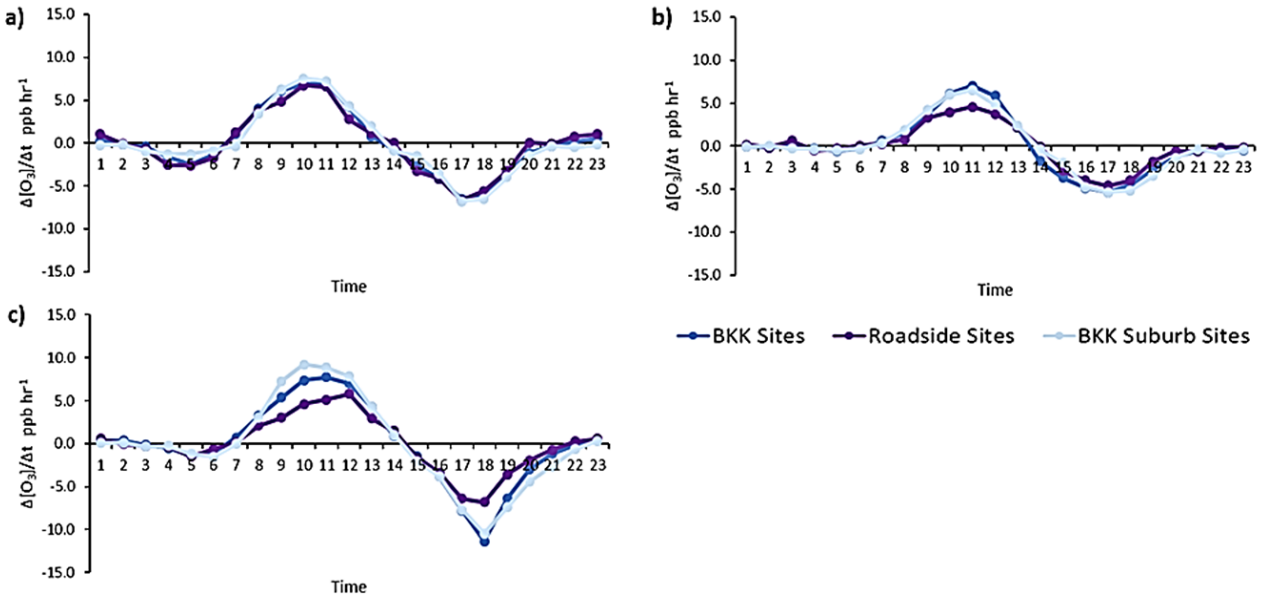


Figure 4: Diurnal variations of rate of change of O_3 concentration ($\Delta[O_3]/dt$) during a) local summers b) wet seasons and c) local winters.

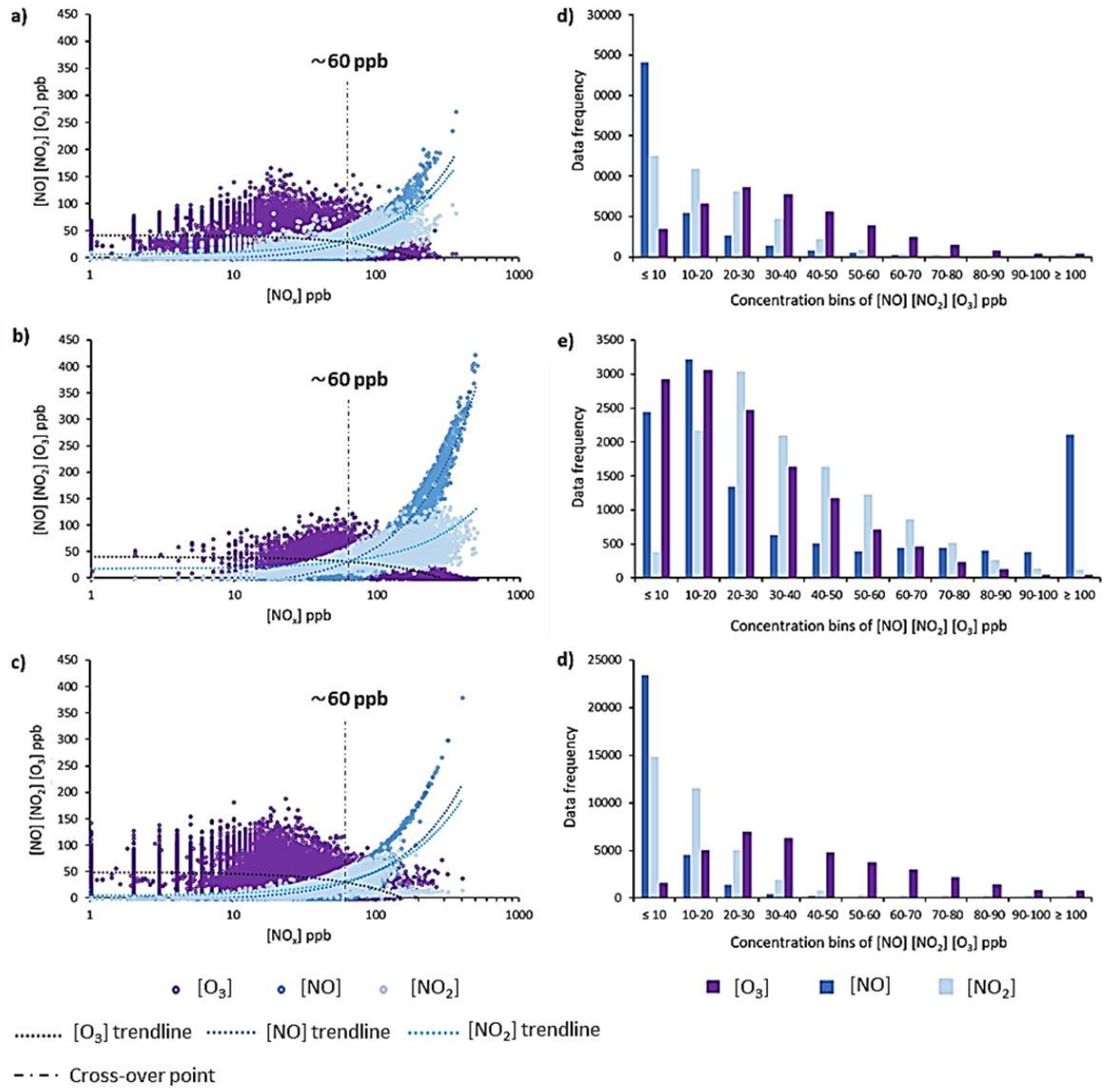
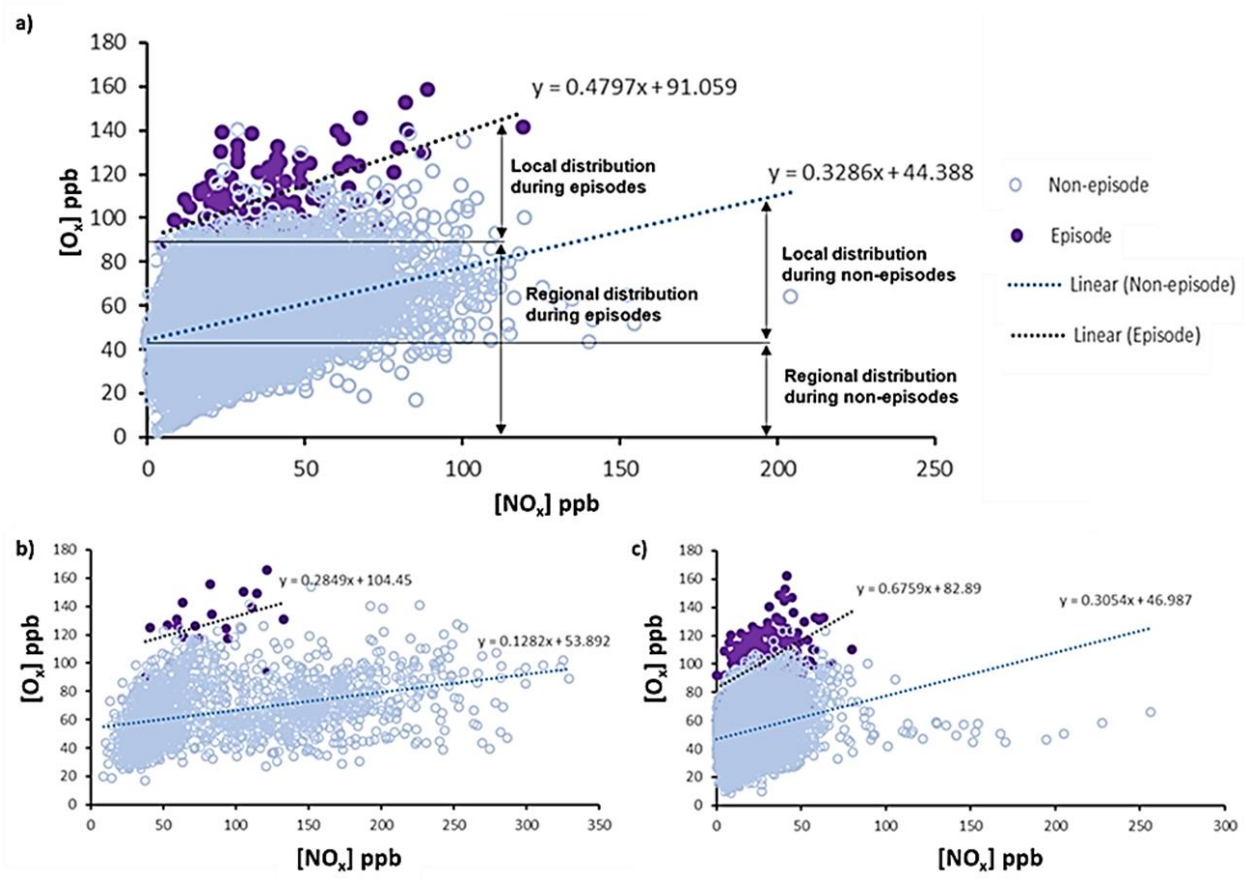


Figure 5: Relationships and crossover points of NO, NO_2 and O_3 at a) BKK sites b) roadside sites and c) BKK suburb sites; and concentration distributions of those species at d) BKK sites e) roadside sites and f) BKK suburb sites.



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590 **Figure 6:** Effects of local and regional contributions on O_x during non-episode and episode days at a) BKK sites, b) roadside sites
591 and c) BKK suburb sites.

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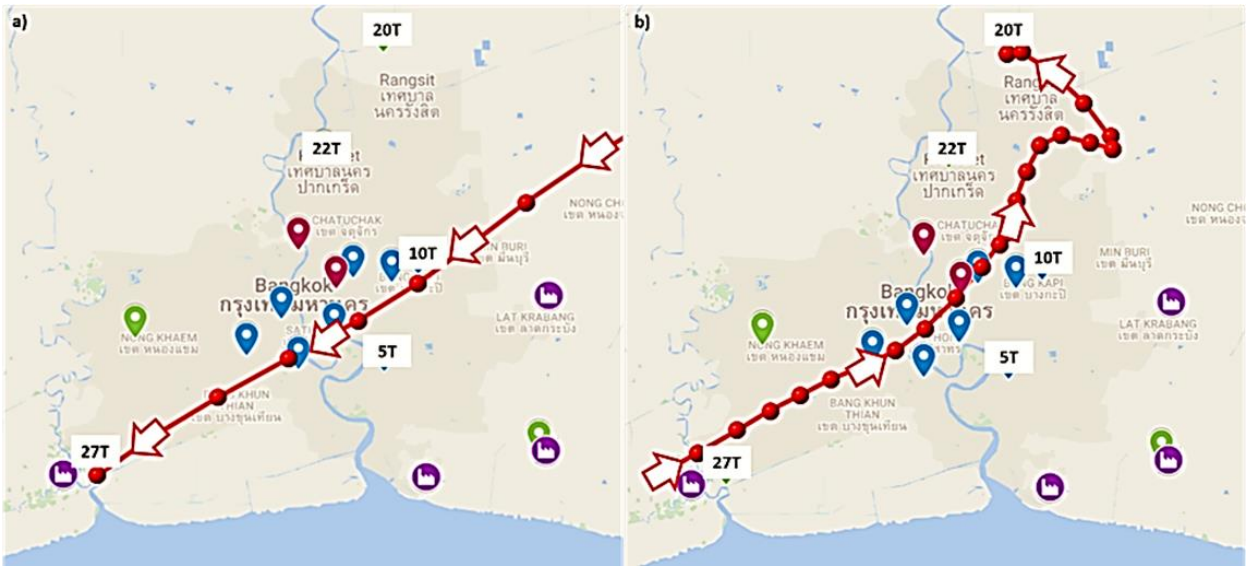
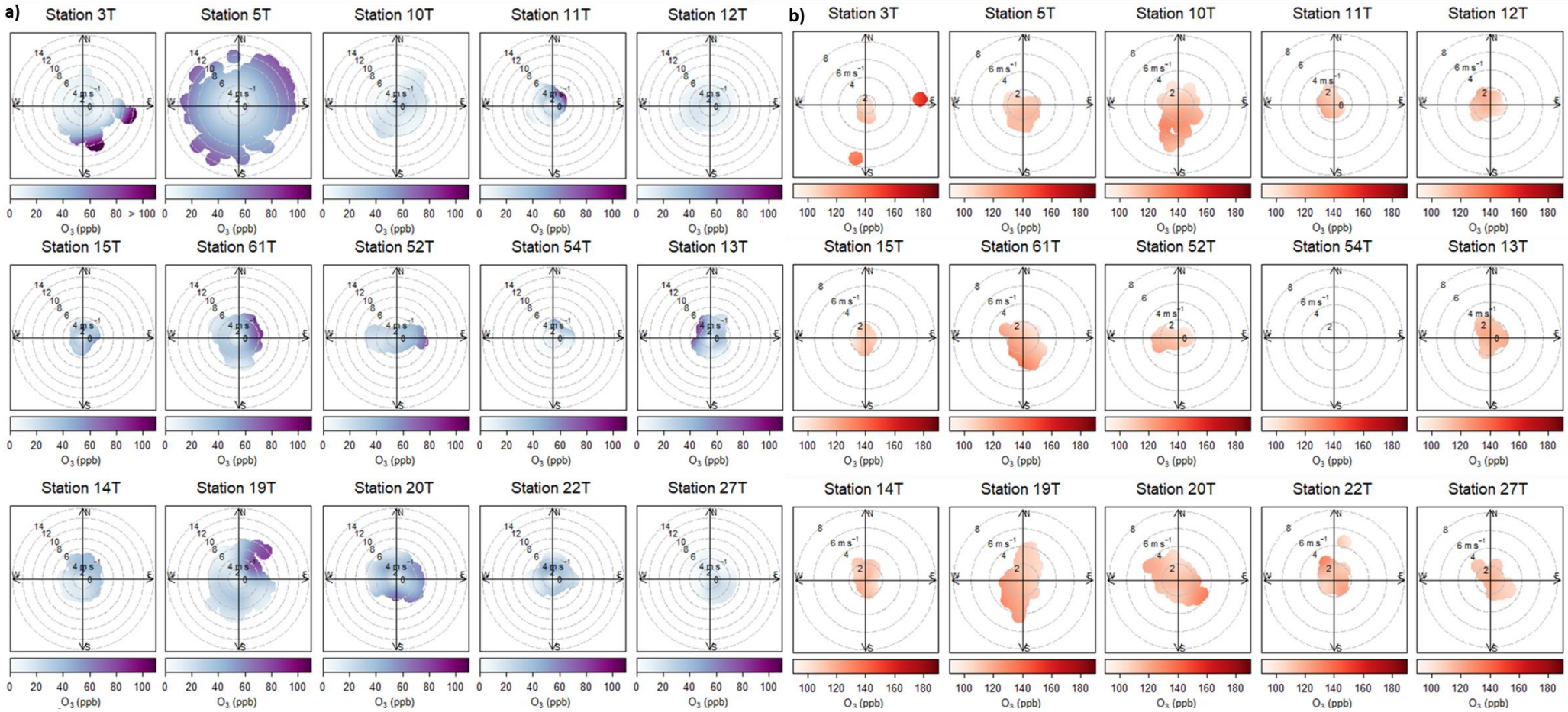


Figure 7: Backward trajectories from HYSPLIT model reveal a) NE wind direction (Jan 13, 2010) and b) SW wind direction (Jan 1, 2010)



623 **Figure 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 ($[O_3]_{hourly} \leq$
624 100 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.

	Non-Episode	Episode
This study		
-BKK sites	$[O_x] = 0.33[NO_x]+44.39$	$[O_x] = 0.48[NO_x]+91.10$
-Roadside sites	$[O_x] = 0.13[NO_x]+53.89$	$[O_x] = 0.29[NO_x]+104.45$
-BKK suburb sites	$[O_x] = 0.31[NO_x]+47.0$	$[O_x] = 0.68[NO_x]+82.89$
UK*	$[O_x] = 0.097[NO_x]+38.2$	$[O_x] = 0.112[NO_x]+55.5$
Buenos Aires, Argentina**	$[O_x] = 0.099[NO_x]+22.0$	
Delhi, India***	$[O_x] = 0.54[NO_x]+28.89$	

Note: *Clapp and Jenkin (2001), **Mazzeo et al. (2005), ***Tiwari et al. (2015)

Table 2: The comparison of CO/NO_x and SO_2/NO_x ratios from this study with other studies (modify from Rasheed et al., 2014).

Region	Source	CO/NO_x	SO_2/NO_x
This study		**19.8**	**0.1**
- *BKK sites*		18.25	0.09
- *Roadside sites*		21.15	0.11
- *BKK suburb sites*		19.20	0.09
Eastern US		4.3	0.94
	Mobile	8.4	0.05
	Point	0.95	1.8
Pennsylvania		2.6	1.7
	Mobile	7.8	0.05
	Point	0.8	2.3
Western US		6.7	0.41
	Mobile	10.2	0.05
	Point	1.2	1.1
Denver Metropolitan		7.3	0.19
	Mobile	10.5	0.05
	Point	0.18	0.44
Raleigh, NC		16.3	0.73
New Delhi, India		50	0.58
Guwahati and Nagpur, India***			> 0.3
Kolkata, and Durgapur, India***			≤ 0.13
Madrid City, Spain*		13.3	0.29
Rouen City, France**		12-18	
Islamabad, Pakistan			
- *Based on Emission Inventory, 2010*	Mobile	4.94	0.34
	Point	0.63	7.0
- *Based on Ambient Data*		10	0.01

* Fernandez-Jiménez et al., 2003

** Coppalle et al., 2001

*** Mallik and Lal, 2014

663 **Table 3:** Number of hours that were found in different AQI categories of O_3 over the BMR during 2010 to 2014

AQI	Hour														
	BKK sites							Roadside sites		BKK suburb sites					
	3T	5T	10T	11T	12T	15T	61T	52T	54T	13T	14T	19T	20T	22T	27T
Good	39018	32021	27959	40715	26606	33628	26442	32665	40231	31070	35429	33592	30793	34301	26873
Moderate	310	713	1023	556	367	479	1178	807	27	1620	944	1687	1340	1466	719
Unhealthy for Sensitive Group	88	139	225	109	82	108	295	151	0	454	288	515	632	448	218
Unhealthy	19	40	61	30	29	38	85	36	0	195	87	184	209	109	96
Very Unhealthy	0	6	12	0	0	10	26	0	0	59	2	51	28	23	9
Hazardous	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

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