Assessment of Gaseous 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, SO_2 and NO_2 were mostly in the National Ambient Air Quality Standards (NAAQs) of Thailand, 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. 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 between 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, 2018a). A majority of the country's development has occurred within and around Bangkok (BKK) (13°45' N and 100°85' E), the capital city of Thailand and Bangkok Metropolitan Region (BMR). The BKK is comprised of the five adjacent provinces of BKK (World Bank, 2018a and 2018b). The increase in emissions is due to accelerated growth combined with high photochemical activity, strong solar insolation, high temperatures and high humidity (Kumar et al., 2012). BMR, with these conditions, has begun to experience air quality degradation, in particular, enhanced secondary pollutants. Since 1995, BKK

has experienced exceedances in Thailand NAAQs for particulate matter (PM) and ozone (O_3) (PCD, 2015). The correlation between BMR air pollution and public health has been observed in several published studies. Ruchirawat et al. (2007) reported the children who lived in BKK are exposed to high levels of carcinogenic air pollutants which may 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 ($\geq$ 65 years), is associated with increasing the number of daily hospital visits for cardiovascular diseases. Jinsart et al. (2002, 2012) reported polices and drivers in BKK tended to expose higher level of PM concentrations compared with the general environment, in which the concentrations of PM were already high. Role of atmospheric processes in elevated O_3 in Thailand were reported in several studies. Long-range transport played an important role in increasing O_3 concentration in Thailand. Generally, long-range transports from the Asia continental contained higher O_3 concentrations compared with long-range transports from the Indian ocean (Pochanart et al., 2001). In BMR, local emission and regional transport were the major contributors to high O_3 concentrations and seasonal fluctuations of O_3, respectively (Zhang and Oahn, 2002). In suburban areas of BKK, volatile organic compounds (VOCs) tended to be a potential factor to enhance O_3 concentration (Suthawaree et al., 2012).

The availability and analysis of multi-year measurements of such gaseous pollutants in the BMR will improve our understanding of how they contribute to the air quality of this area. 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 formation. The emissions from industrial activities also dominates the BMR metropolitan area and contributes to the emissions of sulfur dioxide (SO_2) and the formation of particulate matter.

In this study, 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, have been analysed. Chemical and physical processes associated with high O_3 concentrations have been investigated. Since the concentrations of nitrogen oxide (NO_x) was measured at most of the monitoring station, therefore, O_3 precursors in this study is referred to NO_x. The photochemical reaction 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 the monitoring stations in this study and major monsoon winds over the region. BMR refers to BKK and the five adjacent provinces, including Nakhon Pathom, Pathum Thani, Nonthaburi, Samut Prakan, and Samut Sakhon. These provinces are closely 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). For example, 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, 2016d).

2.2 Data Collection and Data Analysis

Over the four-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 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 is provided in Figure I, supplement material.

Gaseous species were measured at 3m 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 are performed using Excel 2016. Predominant wind directions related to O_3 concentrations are performed using Openair package (tool for the analysis of air pollution data) on RStudio program.

3. Result and Discussion

3.1 Status of Pollution in BMR during 2010 to 2014

Figure 2 a) to e) shows the maximum and average concentration 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 (~22.0±19.8 ppb) and following by BKK sites (17.9±16.9 ppb) and roadside sites (13.3±12.7 ppb). The maximum and average of gaseous pollutants the three monitoring types are provided in Table I, supplement material.

The seasonal variations of the gaseous pollutants reveal that, in general, elevated concentrations were observed during dry season and those decreased during wet season (Figure II, 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 (Figure III, supplement material).

An O_3 exceedances 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 than 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 3 a) to c). The diurnal variations of O_3 show a single-peak pattern (Aneja et al., 2001) with the concentrations increased 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 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 to 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 ~3 ppb (both peaks) at BKK sites, ~3 ppb (both peaks) at roadside sites, and ~6 ppb ~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, supplement material.

Figure 4 a) to c) shows diurnal variations of rate of change of O_3 concentration ($\Delta[O_3]/dt$) during dry season (local summer and local winter) and wet season 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 season, 6.7 to 7.5 ppb hr^{-1} during local summer, and 5.7 to 9.2 ppb hr^{-1} during local winter. 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 site, 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)

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

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

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

During dry season, the values of j_1 and k_3 ranged from 0.12 to 1.22 min^{-1} and 28.3 to 30.9 ppm^{-1} min^{-1}, respectively. The ratio of [NO_2] and [NO] was ~1.9. 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 average 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 are provided in Table II, supplement material.

Figure 5 a) to c) shows the relationships between NO, NO_2 and O_3, their crossover points, and the 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

232 contribution or NO_x-independent refers to the background concentration of O_x that is not
233 influenced by changes of the local pollutants (Clapp and Jenkin, 2001; Tiwari et al. 2015).

234 Figure 6 a) to c) shows the local and regional contribution of O_x at the three monitoring
235 station types. The effects of the local and regional contributions to O_x concentration are analysed
236 by plotting O_x concentrations against NO_x concentrations and fitting the plot with a linear
237 regression ($y = mx + c$). The concentration of NO_x and O_x are referred by x and y, respectively.
238 The slope of the linear regression (m) implies the local contribution and the intercept with the y-
239 axis (c) implies the regional (background) contribution (Aneja et al., 2000; Clapp and Jerkin, 2001;
240 Notario et al., 2012). Table 1 shows the comparison between the fitted linear regressions from this
241 study with other studies. The average background O_x concentrations over BMR during non-
242 episodes ($[O_3]_{hourly} < 100$ ppb) and episodes ($[O_3]_{hourly} > 100$ ppb) were ~48 ppb and ~95 ppb,
243 respectively. The local and regional contributions during the episode days, in general, were about
244 double of those during the non-episode days. The results reveal that elevated O_3 concentrations
245 during the episode days are influenced by both the local and regional contributions of O_x. It is
246 noteworthy that the pattern of the local and regional contributions at roadside sites during non-
247 episode period is composed of two NO_x concentration regimes. The low NO_x regime ($NO_x < 60$
248 ppb) resembles the local and regional contributions during non-episode over BKK suburb sites.
249 The high NO_x regime ($NO_x > 60$ ppb) may represent typical characteristic of air quality near roads.

250 The local contributions from the fitted linear regressions are compared with the local
251 contribution that is calculated from delta O_3 method. A delta O_3 (ΔO_3) analysis was performed to
252 reflect on the intensity of O_3 production in BMR area (Lindsay and Chameides, 1988). Lindsay et
253 al. (1989) analysed high-O_3 events in Atlanta, GA, and showed that rural background O_3 during
254 high O_3 concentrations ($[O_3] > 80$ ppb) in Atlanta Metropolitan Area were higher than its average
255 and the concentration of O_3 increased from ~15 to 20 ppb when the air mass travelled across the
256 city. This enhanced the total O_3 concentration to 80 to 85 ppb. In our study, during the different in
257 the concentrations of O_3 at the upwind and downwind monitoring stations (20T and 27T
258 monitoring station) are averaged. The conditions to calculate ΔO_3 in this study are 1) high O_3
259 concentrations ($[O_3] > 80$ ppb) were observed at least one of the two monitoring stations 2) the
260 calculation is performed 10:00 to 16:00 LT, during dry season to avoid accumulation of air
261 pollutants by surface inversion and effects of the removal process by wet deposition 3) National
262 Oceanic and Atmospheric Administration (NOAA) HYSPLIT model backward trajectories

revealed N-NE, S-SW wind directions (Figure 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/NO_x and 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. Correlation plots among species are provided in Figure V, 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. 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 (low wind speed), elevated O_3 concentrations were observed (Sahu et al., 2013a, 2013b).

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 are 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 "AQI for O_3 calculation", 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

318 analysis (Aneja et al, 2001). The results from this study revealed evidence of violations for O_3 for
319 air quality. This resulted in adverse health effects, human welfare, economics and environment
320 over BMR. Source analysis suggests the first priority should be controlling pollution emissions
321 from local sources that emit primarily from mobile sources. The complexity between O_3 and its
322 precursors and the effects of pollution transport shows that decreasing only NO_x emissions and/or
323 local emissions may not be an effective policy to reduce O_3 since regional air pollution transport
324 i.e. ozone and its precursors contribute to O_3 exceedances. To identify the proportional
325 contribution between local and regional sources of O_3 concentrations during selected O_3 episode
326 days, atmospheric modelling is needed to quantify various processes that contribute to the ambient
327 concentration at specific locations. This scientific analysis provides a frame work for the process
328 of establishing an air quality policy while developing socioeconomic impacts.

329 **4. Conclusion**

330 Among measured gaseous criteria pollutants, O_3 is the only species whose concentrations
331 frequently exceed the NAAQs of Thailand. The O_3 exceedances occur during the dry season (local
332 summer and local winter) and most frequently occur over BKK sites and BKK suburb sites than
333 roadside sites. On average, the number of hourly O_3 exceedances at BKK sites, roadside sites and
334 BKK suburb sites were ~16 hours $year^{-1}$, ~9 hours $year^{-1}$ and ~43 hours $year^{-1}$, respectively. The
335 lower number of O_3 exceedances at roadside sites demonstrates the effects of the titration of O_3 by
336 NO, due to, high concentrations of NO that were generally observed at this monitoring type
337 (average $[NO]_{hourly}$ = ~166.0±19.8 ppb). Under photostationary state assumption, during dry
338 season, the values of reaction rate coefficient of photochemical reaction of NO_2 (j_1) and reaction
339 rate coefficient of chemical reaction between NO and O_3 (k_3) range from 0.12 to 1.22 min^{-1} and
340 range from 28.3 to 30.9 ppm^{-1} min^{-1}, respectively. NOx values of about 60 ppb, marks the threshold
341 for the interconversion between O_3, NO and NO_2. Under the low NO_x regime ($[NO_x] < 60$ ppb),
342 O_3 is the dominant species; on the other hand, under the high NO_x regime ($[NO_x] > 60$ ppb), the
343 concentrations of O_3 rapidly decrease. The decrease of O_3 under the high NO_x regime describes
344 the important role of NO in destroying O_3 in the atmosphere in polluted environments. The local
345 and regional contributions of O_x concentrations, under stagnant condition (wind speed < 4 m s^{-1})
346 and predominant wind directions (northerly, southerly and westerly winds) associate with elevated
347 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.

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Competing Interest

The authors declare that they have no conflict of interest.

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Figures:

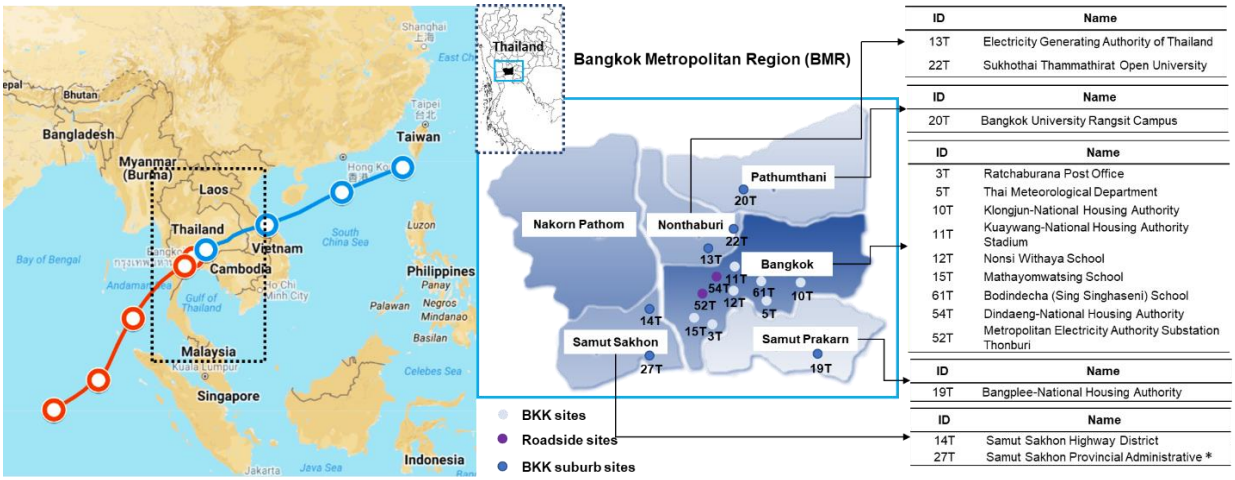
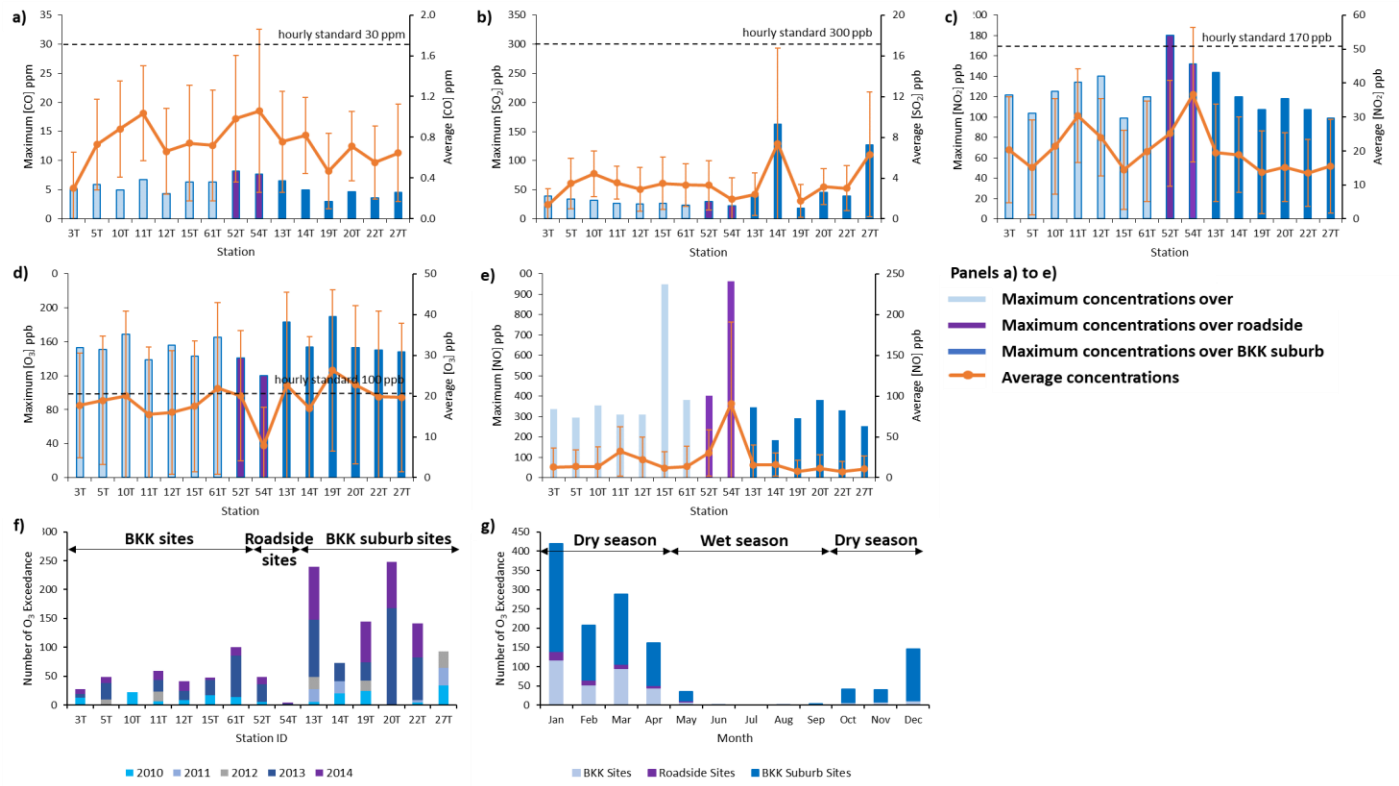


Fig. 1: Map of BMR, monitoring station locations and two major monsoons winds (from NOAA HYSPLIT back trajectory model). Three monitoring station types, including BKK sites, roadside sites and BKK suburb sites are shown in light blue dots, purple dots and blue dots, respectively. (Note: * the station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



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520 **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
521 from the 15 monitoring stations, during 2010 to 2014, are compared with the hourly NAAQs (dotted line) of Thailand
522 (except NO which is not a criteria pollutant). The number of hourly O_3 exceedances are shown by f) locations and g)
523 seasons.

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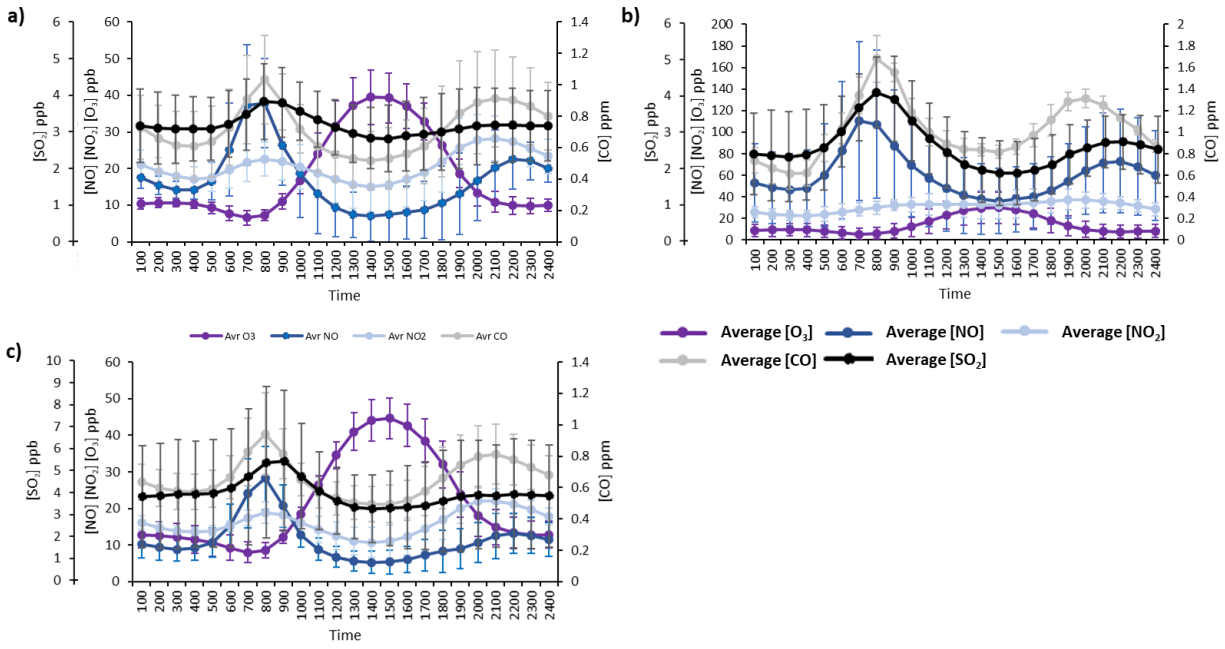


Fig 3: Diurnal variations of gaseous species including O_3, NO, NO_2, CO and SO_2 at a) BKK site b) roadside sites and c) BKK suburb sites.

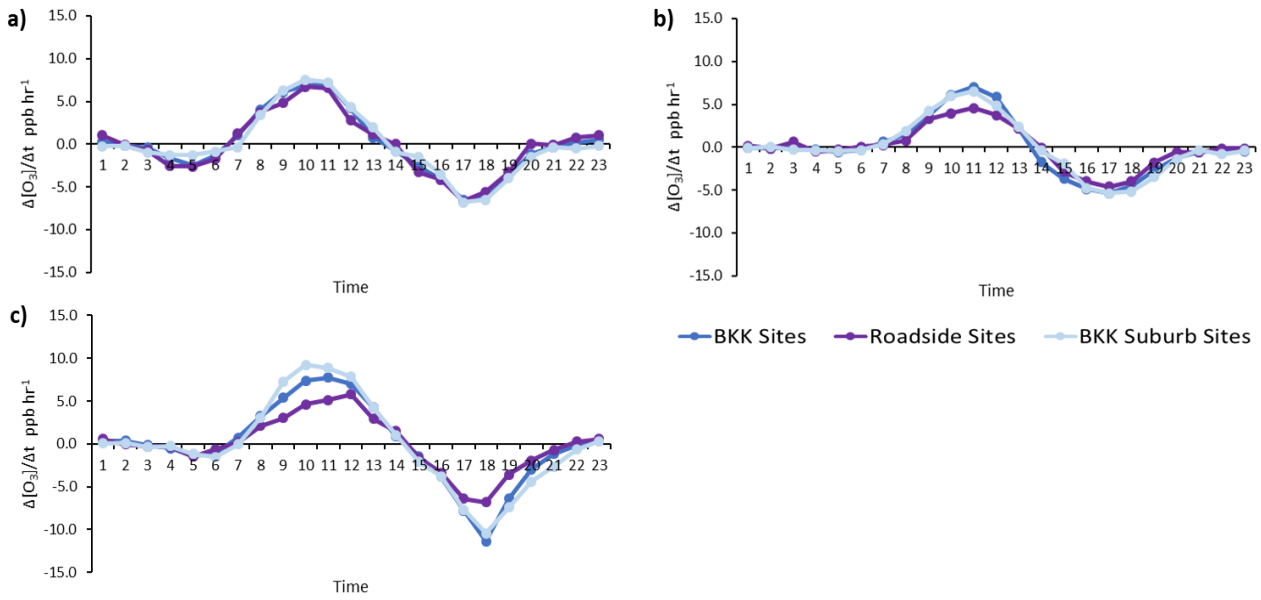


Fig. 4: Diurnal variations of rate of change of O_3 concentration ($\Delta[O_3]/dt$) during a) local summer b) wet season and c) local winter.

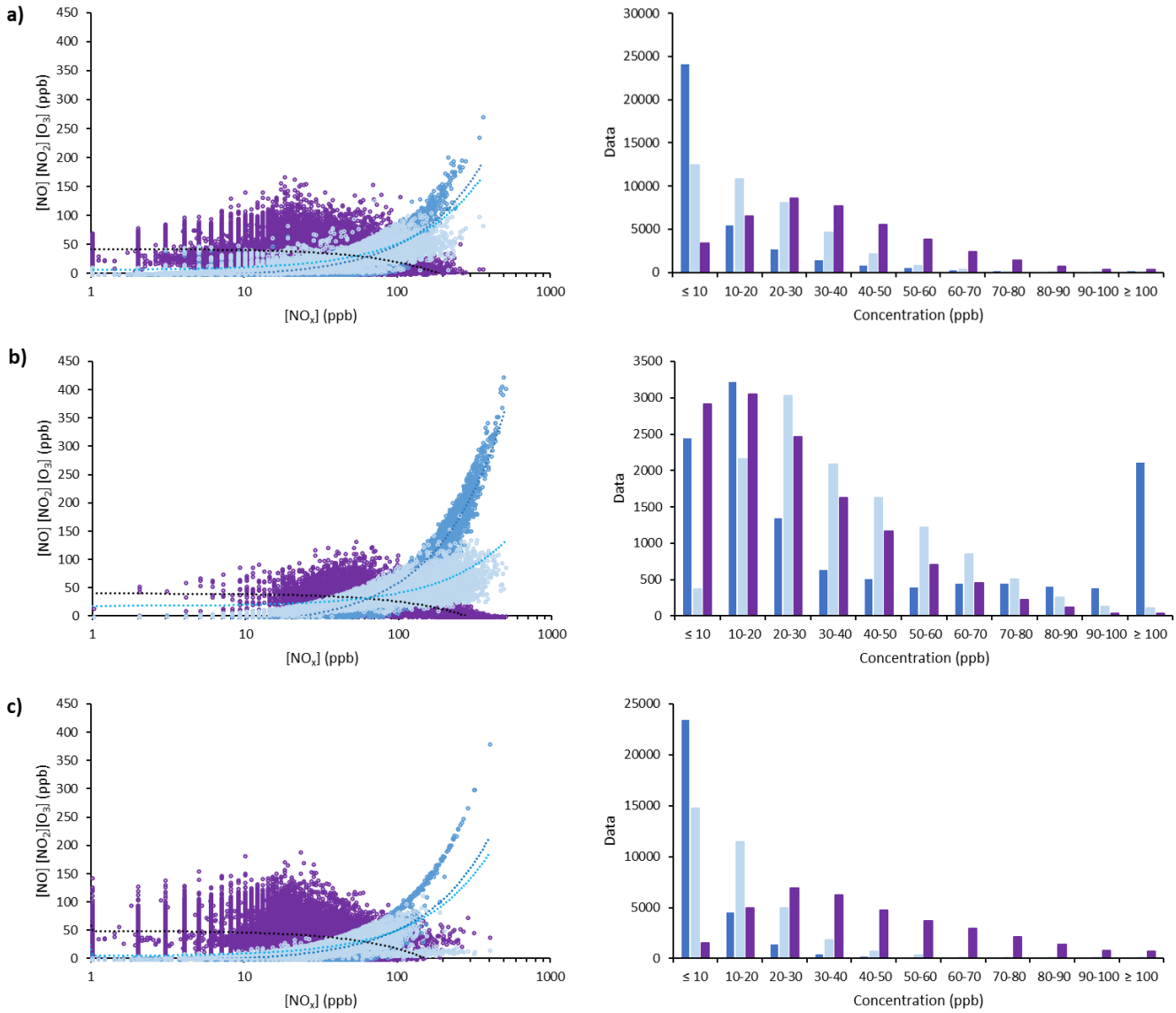
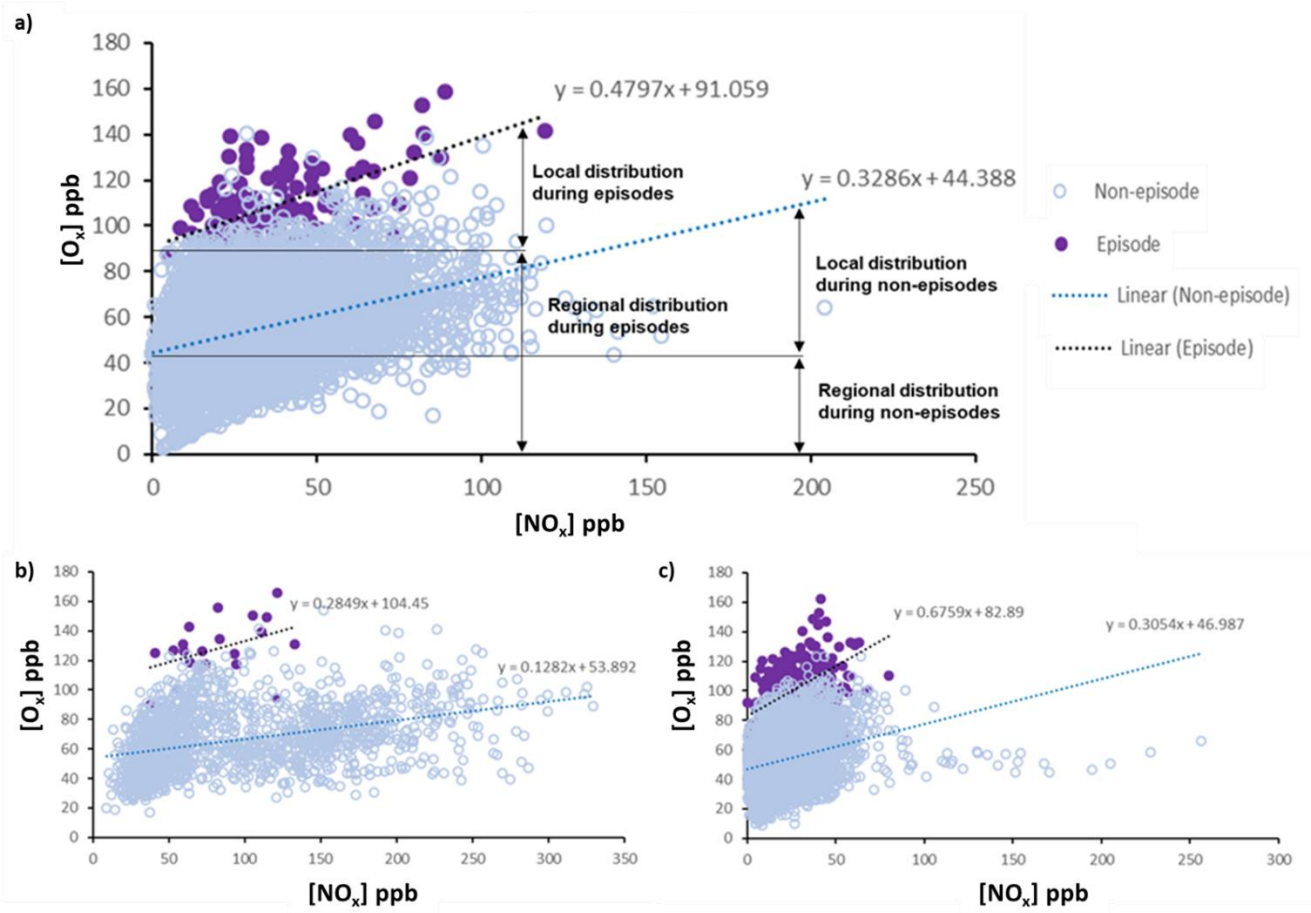


Fig. 5: relationship, crossover point and concentration distribution of NO, NO_2 and O_3 at a) BKK sites b) roadside sites and c) BKK suburb sites.



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

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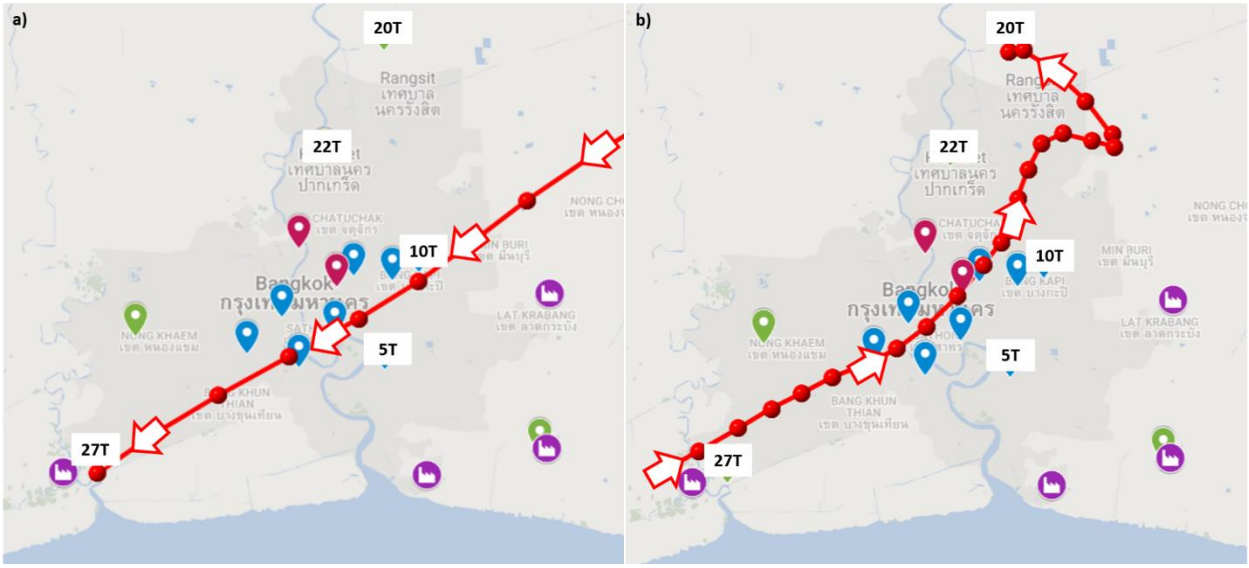
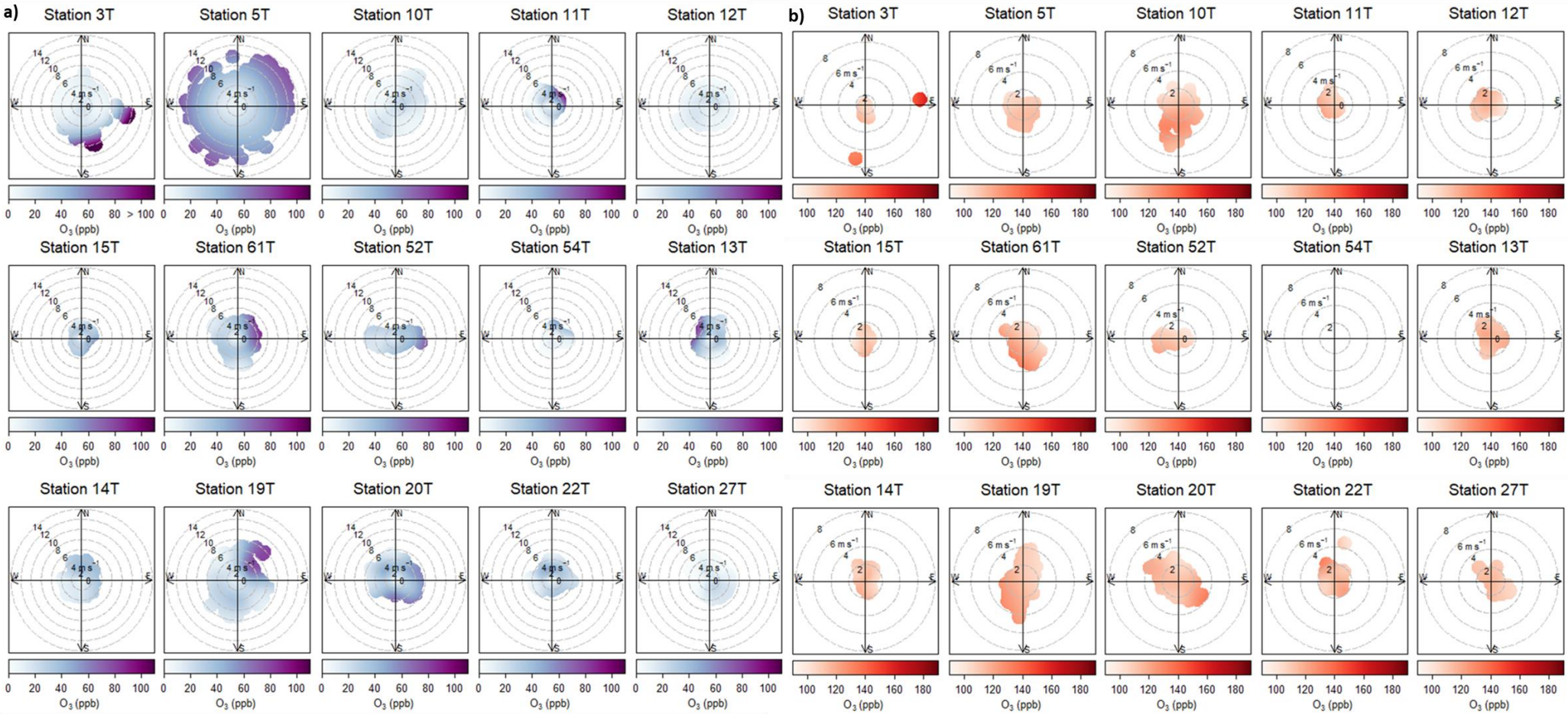


Fig. 7: Backward trajectories from HYSPLIT model reveal a) NE wind direction (Jan 13, 2010) and b) SW wind direction (Jan 1, 2010)



586 **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

587 ($[O_3]_{hourly} \leq 100$ ppb), over BMR during 2010 to 2014.

Tables:

Table 1: the comparison of fitted linear regression from this study, including from BKK sites, roadside sites, and BKK suburb sites with 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***	$[O_x] = 0.54[NO_x]+28.89$	

*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

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