Response to Reviewers Comments
Assessment of Gaseous Pollutants in Bangkok Metropolitan Region, Thailand
Pornpan Uttamang, Viney P Aneja, Adel Hanna

Ref: acp-2017-1063

We wish to thank the reviewers for the careful and thoughtful review of our manuscript. We appreciate reviewer 2’s comments “Overall, the article is well written and examines the interaction of Ozone with NOx regime. The analysis was well done.” All the comments and suggestions are now incorporated in the manuscript.

Reviewer #1
General Comment:
Pornpan Uttamang et al. have presented observations of CO, NOx, SO2 and O3 from 15 monitoring sites at understudied Bangkok Metropolitan Region (BMR) for a fiveyear-long period from 2010-2014. Background pertaining to the air-quality in terms of PM and O3 exceedance events in the BMR is provided. However, the authors do not mention the knowledge gap or scientific question that they want to address from this study. I have major concerns with the paper which include description of analytical methods and discussion about quality control (calibration and sampling protocols, filter criteria) of dataset used. The statistical analysis is also weak which mostly covers average/maximum over the entire study periods, without going into details of specific seasons, inter-annual trends and pin-pointing the season-specific emission sources/formation processes and removal processes of the pollutants. The conclusions are drawn either from the regression lines having poor fit parameters or oversimplification of methods for source identification available in the peer-reviewed literature. The manuscript needs to address the major concerns (highlighted in specific comments) before it can be considered further. After performing the analysis suggested in the specific comments, corrections and restructuring the paper, the scientific outcome might be significantly different from the present version and should be considered as a new publication.

Authors’ response: Thank you. The last paragraph of the Introduction (line 17 – 24) succinctly provides both the knowledge gap and scientific question being addressed. We have now made the statistical analysis more robust based on reviewer’ suggestions.

Specific Comments:

Title: Authors might consider making the title of the paper more specific. Authors assess CO, NOx, SO2 and O3 air pollution and not overall air pollution in general.

Authors’ response: Thank you. We have now modified the title to “Assessment of Gaseous Pollutants in Bangkok Metropolitan Region, Thailand”

Introduction: The authors have included a description of auto-mobile fleet and manufacturing industries in the introduction which should rather be a part of the site description. The
introduction is poorly structured. Authors should include a brief literature review of the previous works from BMR, outlook from these studies and what are the knowledge gaps they want to address from this paper.

The authors should also mention, why they have chosen to study CO, NOx, SO2 and O3. At-least a line each about their importance regarding atmospheric chemistry and air quality should be present. The authors have referred to Zhang and Oanh, [2002] for the site description. However, the findings there should also be mentioned in the introduction, as Zhang and Oanh, [2002] have analyzed monthly and diel variation, O3 exceedances, drivers for high ozone episodes and relationship of ozone production with NOx/NMHC ratio. These are quite relevant for the present study. Similarly, the work of Pochanart et al., [2001] should be highlighted in the introduction. I found few other studies (mentioned below) which are relevant to the present work and should be highlighted in the introduction. There might be several more!


Authors’ response: Thank you. We have now modified the Introduction to include the discussion in the references provided by the reviewer.

Page 2, Line 23: Authors state “possible emission sources of pollutants that associate with O3 formation are identified”. However, such identification is not discussed in the manuscript. Authors have only used the ratio of CO/NOx and SO2/NOx to identify whether the emission sources are mobile or point in nature. The method itself has an inherent limitation which is mentioned later in the specific comment for the section.

Authors’ response: Thank you. We have now modified the Introduction. Please refer to our discussion in the comment “Section 3.5 Page 11, Line 16” below.

Methodology: The exact measurement period should be mentioned in this section. This paper discusses a five-year-long measurement period and shows data over 15 different measurement stations and authors should provide a time-line for data availability for each station.

Authors’ response: Thank you. We have now provided the measurement period in the modified manuscript and provided a time-line for data availability for each station as part of the supplement material.
Page 3, line 22: What is the basis of the assumption that monitoring sites used were representative of BMR specific patterns and trends?

Authors’ response: Thank you. Based on the reviewer, we have modified the manuscript by removing the sentence.

Data Collection and Data Analysis: I have major concerns with this section. Authors did not provide any sampling details. The trace gas analysers for CO, NO\textsubscript{x}, SO\textsubscript{2} and O\textsubscript{3} are known to have drifts with time. Authors mention that equipment and monitoring stations are calibrated every year. This is not enough. There should be frequent zero drift check for CO (at-least daily) and for NO\textsubscript{x}, SO\textsubscript{2} and O\textsubscript{3} (at-least once a week). The linearity of the detection should also be checked with calibration experiments performed at-least once a month. The authors did not provide any information about the drift in the sensitivity of instruments over the period of 5 years. Detection limits of the trace gas analysers and uncertainties of the measurements should also be provided.

Authors’ response: Thank you. As indicated in the manuscript, the data were collected, and after QA/QC, were provided by the Pollution Control Department (PCD), Thailand. Data loggers are calibrated/ checked at least every 15 days. Air inlets are cleaned at least every 15 days. Equipment is single-point calibrated and multi-point calibrated at least every 15 days and at least every 3 months. Monitoring stations and equipment are audited by external auditors every year. We have modified our manuscript to make a clarification.

Page 4, line 6: Authors mention that quality assurance and quality control on the dataset were performed by PCD prior to receiving the data. What are these quality controls?

Authors’ response: Thank you. QA/AC protocols are published in the PCD, Thailand government document.

Page 4, line 9: What are the manual quality controls? What are the criteria for choosing unusual observations?

Authors’ response: Thank you. QA/AC protocols are published in the PCD, Thailand government document. However, we did not provide any additional guidelines for data collection.

Result and Discussion

Section 3.1: Authors have only provided maximum and average over the entire five-year period. Since they have continuous one hour time resolution dataset from 15 monitoring stations for a five year long period, authors should also include inter-annual variability and seasonal statistics at-least for different monitoring station types. Given the advantage of also having wind speed/ wind direction data, authors should consider comparing various airmass fetch regions for some monitoring sites. For ozone, it makes more sense to separate daytime and night-time before reporting the average concentrations. The authors discuss extensively about 1-hour exceedance of ozone concentrations, but there is no description of how are these exceedance events calculated.
One cannot compare the hourly average concentrations directly with the NAAQS. What about the ozone exceedance from 8-h standard? Bangkok air quality standard provides criteria for both 1-hour and 8-hour average ozone. 8-h average is intended to provide a better protection from long term ozone exposure.

**Authors’ response:** Thank you. We have now provided inter-annual plots and seasonal variation plots for gaseous criteria pollutants from the monitoring stations. In the plots, we have averaged the data for each monitoring type station (from BKK sites, roadside sites and BKK suburb sites). This figure is now included in the supplementary material. However, the discussion associated with this information is now included in the manuscript. Moreover, we have now included the average concentrations of O$_3$ during daytime (6:00 AM to 6:00 PM) and during nighttime (6:00 PM to 6:00 AM) in the modified manuscript.

With regards to segregating wind direction data we performed a more robust back trajectory analysis. Moreover, we provided wind-rose plots for each of the monitoring stations and discussed it in the manuscript.

The National Ambient Air Quality Standards of Thailand provides hourly and 8-hour average standards of O$_3$ (0.10 ppm and 0.07 ppm, respectively). In this study, we compared the hourly concentrations of O$_3$ with the hourly O$_3$ standard in order to examine number of O$_3$ exceedances. To study the effects of O$_3$ on human health, we applied Air Quality Index (AQI) of O$_3$ instead of using the O$_3$ exceedance from 8-hour standard, which we believe that, using AQI of O$_3$ will provide more advantages than using the O$_3$ exceedance from 8-hour standard. Since AQI of O$_3$ is categorized into six categories, with four of the six categories providing the information of the severity of high O$_3$ concentrations on human health, from sensitive groups to healthy people; therefore, applying AQI for O$_3$ will provide better information for air quality management.

**Section 3.2 Diurnal Variation of the Gaseous Species:** Regional meteorology has strong influence on primary emission processes, production of secondary pollutant e.g. ozone and ambient concentrations of pollutants. I would recommend season wise analysis of diel variation of gaseous species. For example, the authors can refer to the work of Gaur et al. [2014] and Kumar et al. [2016]. This would also enable to identify the periods when ozone production is maximum during the year. Authors should also analyse, how does rate of formation of ozone from sunrise until it attains the peak daytime values changes at different sites and in different seasons. Authors could refer to the work of Naja and Lal [2002].


Authors should provide an explanation for why a second peak is not observed in the diel profiles of SO\(_2\) at all sites. In line 20 of page 7, authors speculate that SO\(_2\) is emitted by automotive diesel engine exhaust. If we observe the diel profile of NO from the BKK sites, a bimodal profile is observed which is attributed to traffic emissions. Moreover, even if we assume that manufacturing facilities point sources are the SO\(_2\) contributors as mentioned in line 23 of page 11, their emission strength would not vary over the time scale of a day and a bimodal profile driven by boundary layer meteorology should be observed.

Similarly, authors should also provide an explanation for the relatively flatter diel profile of NO\(_2\) at roadside sites.

**Authors’ response:** Thank you. We have now provided season wise analysis of diel variation of gaseous species for the three monitoring station types in the supplementary material and a discussion is provided in the manuscript.

We have also provided the rate of change of O\(_3\) concentration (Naja and Lal, 2002) during the three seasons and in the three monitoring station types with explanation in the modified manuscript.

For the diurnal variations of SO\(_2\), in the manuscript, we explained that “…The concentrations of SO\(_2\) increase again in the afternoon and reach a second-peak around 21:00 LT over roadside sites. Over BKK sites and BKK suburb sites, the concentrations of SO\(_2\) are nearly constant after 19:00 LT…” which the second peak of SO\(_2\) were observed over three monitoring station types, but the magnitude of the concentrations of SO\(_2\) over BKK sites and BKK suburb sites were small. For the diurnal variation of NO\(_2\), at the roadside sites also showed a bimodal distribution, but flatter than those at other sites. However, we have now included the clarification and explanation in the manuscript.

**Section 3.3 Interconversion between O\(_3\), NO and NO\(_2\) and Photochemical Reaction:** I have major concerns again with this section. In line 23, authors mention “the photostationary state (PSS) is applied through all chemical reactions for O\(_3\) formation during 10:00-16:00 LT”. However, later in the section they assume photostationary state only between O\(_3\), NO and NO\(_2\). In polluted environments, RO\(_2\) and HO\(_2\) also oxidize NO to NO\(_2\) and hence disturb the PSS of NO, NO\(_2\) and O\(_3\) [Mannschreck at al., 2004]. Hence the \(j_1\) values calculated by only considering O\(_3\), NO and NO\(_2\) in the PSS would not be accurate.

Mannschreck, K., Gilge, S., Plass-Duelmer, C., Fricke, W., and Berresheim, H.: Assessment of the applicability of NO-NO2-O3 photostationary state to long-term measurements at the Hohenpeissenberg GAW Station, Germany, Atmos. Chem. Phys., 4, 1265-1277, 10.5194/acp-4-1265-2004, 2004.

Moreover, \(j_1\) values are strongly dependent on incoming solar radiation and mentioning an average over 10:00 L.T. until 16:00 L.T. will be oversimplification. In the moderately polluted environment, the photostationary state between O\(_3\), NO and NO\(_2\) is achieved within 60 s to 300 s during daytime [Trebs et al., 2012]. Authors should perform a calculation of \(j_1\) at similar timescales.

Trebs, I., Mayol-Bracero, O. L., Pauliquevis, T., Kuhn, U., Sander, R., Ganzeveld, L., Meixner, F. X., Kesselmeier, J., Artaxo, P., and Andreae, M. O.: Impact of the Manaus urban plume on

I cannot understand, why the authors emphasize the calculated $k_3$ values. It depends on a single parameter which is temperature! Do the authors want to show that their temperature measurements are reasonable or their calculation is accurate? Next, the authors are using O$_3$ measurements to estimate the $j_1$ values and again using $j_1$ to explain high O$_3$ concentration at some sites. This is cyclic. Polynomial trend lines are used to investigate the interconversion between O$_3$, NO and NO$_2$. However, as seen from Figure 4, The fit is very poor for O$_3$ in all the three cases. So inference drawn using these fits would not be conclusive.

Authors’ response: Thank you. In our study, we evaluated the relationship between O$_3$ with the gaseous criteria pollutants for the NAAQs of Thailand. The assumption of the photostationary state (PSS) ($\phi = 1$), therefore, was applied through the chemical reactions of O$_3$ and NO$_x$ only.

Mannschreck et al., 2004, reviewed the PSS parameter ($\phi$) as:

$$\phi = \frac{j[NO]}{k[NO][O_3]}$$

Where $j$ was the photolysis rate of NO$_2$, and $k$ was the rate of the chemical reaction of NO and O$_3$. In the Mannschreck et al., 2004, when $\phi$ was equal to 1, then other chemical reactions converting NO to NO$_2$ and local emissions of either compound were negligible. However, these cases were rare and were limited to very polluted conditions. On the other hand, peroxy radicals (RO$_2$) played an important role to contribute to additional NO and NO$_2$, under clean or moderately polluted conditions. In the study of Mannschreck et al. (2004), the measurement was performed in a rural site, generally, the site was affected by relatively clean air masses (yearly average of NO$_x$ was below 3.5 ppb). The site was surrounded by forests (70%, mostly coniferous) and agricultural pastures (30%). The distance to the nearest urban and major industrial areas was about 80 km. Furthermore, the study mentioned that “for high NO$_x$ concentrations the levels of peroxy radicals should approach zero, since the sink for RO$_2$ increases with increasing NO and since OH as a precursor for RO$_2$ as well as RO species are removed via reaction with NO$_2$”. Therefore, we believe that the assumption of PSS holds for our study region (e.g. average of hourly concentration of NO$_x$ at BKK sites, roadside sites, and BKK suburb sites were ~30 ppb, ~88 ppb and ~21 ppb, respectively. These NO$_x$ values are far in excess of rural/semi-rural values in the study of Mannschreck et al., (2004)).

With regards to the calculation of $j_1$, it is strongly dependent on incoming solar radiation and on other variables (i.e. the following equation):

$$j_{q,p} = \int_0^\infty 4\pi I_{p,\lambda} b_{a,g,q,\lambda,\tau} Y_{q,p,\lambda,\tau} d\lambda$$

Where
4πI_{p,λ} = Actinic flux

b_{a,g,q,λ,T} = Average absorption cross section

Y_{q,p,λ,T} = Average quantum yield

However, these variables were not measured in our study at the monitoring stations.

With regards to the calculation of $k_3$, our intention is not to emphasize the $k_3$ calculation to show that our temperature measurements were reasonable, but rather to calculate $j_1$. However, we have now modified our manuscript and removed using $j_1$ values to explain O$_3$ concentration.

With regards to the polynomial trend lines, we have now modified the plots by including histogram of the concentrations of O$_3$, NO and NO$_2$ to present data distribution of these species. Generally, most of the records are in low to middle concentration bins.

**Section 3.4**: What are the criteria for differentiation between episodes and non-episodes?

For the linear regression presented in this section, one can observe significant scatter around the fitted line. In some cases, (for example roadside sites, non-episode), one can clearly observe two different regions in the plots and a single linear fit over entire dataset cannot be justified.

For the delta O$_3$ analysis, how were the back trajectories calculated? How many trajectories per day and how many days backward trajectories at what height were calculated? Authors should also provide the number of days/hours when N-NE and S-SE wind directions respectively were observed. How was the agreement between local wind directions and the wind directions derived from NOAA HYSPLIT model? Given the large scatter around average of 10 ppb delta O$_3$, the conclusion of local production is rather week for days with O$_3$ concentrations > 80 ppb. The sentence structuring is poor and was difficult to follow. This also needs improvement. The conclusion regarding crossover points is drawn from polynomial regressions which have very poor fit parameters (and not even mentioned in the paper). The high NOx and low NOx regime should be calculated based on the ratio of NOx OH reactivity and VOC OH reactivity or using model calculated indicators (e.g. CH$_2$O/NO$_x$, H$_2$O$_2$/HNO$_3$ and O$_3$/([NO$_2$]+NO$_x$)) as described by Kumar et al., [2011]. Classification based on cross over points are an oversimplification of the polynomial fits.


**Authors’ response**: Thank you. We had explained that an O$_3$ episode was identified when hourly O$_3$ concentrations were greater than 100 ppb (the O$_3$ NAAQs for Thailand).

With regards to the linear regression, we presented “the estimation” of local and regional contributions of O$_3$. Furthermore, we also compared the result from our study to results from other studies (using similar linear regression method).
For the two different observed NO\textsubscript{x} regions at roadside sites, we provided in our discussion the following “It is noteworthy that the pattern of the local and regional contributions at roadside sites during non-episode period is composed of two NO\textsubscript{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”.

To estimate the local and regional contribution by plotting O\textsubscript{x} against NO\textsubscript{x} were reported in several published studied, for example Clapp and Jenkin (2001), Aneja et al., (2001), Mazzeo et al., (2005), Tang et al., (2009), Notario et al., (2012), Rasheed et al., (2014), Tiwari et al., (2015). These studies provide similar plots to our study. All these references are cited in the manuscript.

Clapp, L. J. and Jenkin, M. E.: Analysis of the relationship between ambient levels of O\textsubscript{3}, NO\textsubscript{2} and NO as a function of NO\textsubscript{x} in the UK. Atmospheric Environment, 35(36), 6391- 6405, doi:10.1016/S1352-2310(01)00378-8, 2001.


Mazzeoa, N. A., Venegasa, L. E. and Chorenc, H: Analysis of NO, NO\textsubscript{2}, O\textsubscript{3} and NO\textsubscript{x} concentrations measured at a green area of Buenos Aires City during wintertime, Atmospheric Environment, 39, 3055–3068, doi:10.1016/j.atmosenv.2005.01.029, 2005.


Notario, A., Bravo, I., Adame, J. A., Díaz-de-Mera, Y., Aranda, A., Rodríguez, A., and Rodríguez, D.: Analysis of NO, NO\textsubscript{2}, NO\textsubscript{x}, O\textsubscript{3} and oxidant (Ox = O\textsubscript{3}+NO\textsubscript{2}) levels measured in a metropolitan area in the southwest Iberian Peninsula, Atmospheric Research, 104-105, 217-226, doi:10.1016/j.atmosres.2011.10.008, 2012.


Tiwari, S., Dahiya, A., and Kumar, N.: Investigation into relationships among NO, NO\textsubscript{2}, NO\textsubscript{x}, O\textsubscript{3}, and CO at an urban background site in Delhi, India, Atmospheric Research, 157, 119-126, doi:10.1016/j.atmosres.2015.01.008, 2015.

With regards to the delta O\textsubscript{3} analysis, back trajectory was determined when hourly concentration of O\textsubscript{3} > 80 ppb was observed either at 27T or 20T sites. By performing the backward trajectories using the NOAA HYSPLIT model, we identified the wind directions that related with high O\textsubscript{3} concentrations at both the monitoring stations. We calculated delta O\textsubscript{3} when air masses were observed from NE to SW or vice versa direction (about 200 records during the study period). In general, it should be noted that there is good agreement between the local station wind direction measurement (wind-roses analysis) and the back-trajectory analysis.
With regards to the low and high NO\textsubscript{x} regimes in our manuscript, the low and high NO\textsubscript{x} regimes refer to the concentrations of NO\textsubscript{x} that are either lower or higher than the cross over point i.e. [NO\textsubscript{x}] = 60 ppb (previous studies (Clapp and Jenkin, 2001; Notario et al., 2012; Tiwari et al., 2015) have also suggested similar NO\textsubscript{x} regimes). Furthermore, we do not have CH\textsubscript{2}O, NO\textsubscript{y}, H\textsubscript{2}O\textsubscript{2} and HNO\textsubscript{3} observations. Therefore, our analysis was limited only to NO\textsubscript{x} species. The paper mentioned by the reviewer (Kumar et al., 2012) reported the ratio of CH\textsubscript{2}O/NO\textsubscript{y}, H\textsubscript{2}O\textsubscript{2}/HNO\textsubscript{3} and O\textsubscript{3}/(NO\textsubscript{y} – NO\textsubscript{x}) based on the modeling analysis performed by WRF-Chem model. This modeling analysis is not within the scope of our study.

Clapp, L. J. and Jenkin, M. E.: Analysis of the relationship between ambient levels of O\textsubscript{3}, NO\textsubscript{2} and NO as a function of NO\textsubscript{x} in the UK, Atmospheric Environment, 35(36), 6391- 6405, doi:10.1016/S1352-2310(01)00378-8, 2001.

Notario, A., Bravo, I., Adame, J. A., Díaz-de-Mera, Y., Aranda, A., Rodríguez, A., and Rodríguez, D.: Analysis of NO, NO\textsubscript{2}, NO\textsubscript{x}, O\textsubscript{3} and oxidant (Ox = O\textsubscript{3}+NO\textsubscript{2}) levels measured in a metropolitan area in the southwest Iberian Peninsula, Atmospheric Research, 104-105, 217-226, doi:10.1016/j.atmosres.2011.10.008, 2012.

Tiwari, S., Dahiya, A., and Kumar, N.: Investigation into relationships among NO, NO\textsubscript{2}, NO\textsubscript{x}, O\textsubscript{3} and CO at an urban background site in Delhi, India, Atmospheric Research, 157, 119-126, doi:10.1016/j.atmosres.2015.01.008, 2015.

**Section 3.5 Page 11, Line 16:** A good correlation implies good correlation coefficient (r) for a linear regression and not necessarily a large value of slope. Authors’ logic of having a high CO/NO\textsubscript{x} ratio (slope of fit) because of a better correlation between the two species emitted from point sources is difficult to follow. The authors state that high CO/NO\textsubscript{x} and low SO\textsubscript{2}/NO\textsubscript{x} ratio is characteristic of mobile sources. What are the values they referring to? Is there a threshold? What is the correlation coefficient of the liner regression between CO and NO\textsubscript{x}? Such correlation plots should at-least be provided in supplement. Since the authors have a great advantage of having the data from multiple receptor locations, they should use some statistical source apportionment models (for example, Positive Matrix Factorization (PMF) or the work by Garg and Sinha [2017])


The authors have referred to the work of Parrish et al. [1991] for local source identification using CO/NO\textsubscript{x} ratio. However, longer-lived NO\textsubscript{y} should be used in place of NO\textsubscript{x}. This method can be used for estimating the background concentration of a short-lived species by performing a lognormal regression with a long-lived species. Simply using the ratio of CO and NO\textsubscript{x} to conclude the dominance of mobile source over point sources or vice versa by performing a linear regression over entire dataset of a group of specific monitoring station type will be a wrong over-interpretation of these ratios. This is also evident from the SO\textsubscript{2}/NO\textsubscript{x} ratios reported in Table 3. The SO\textsubscript{2}/NO\textsubscript{x} values are very similar for all the types of sites and even higher for roadside sites as
compared for suburban and BKK sites. Based on authors assertion, it should be minimum for roadside sites among the three categories.

Authors’ response: Thank you. The threshold or value to classify the difference between emissions from mobile sources and point sources has not been quantified definitively, however, the relative magnitude of the ratios provides an insight on source characteristics. We have compared our results with other published studies from different urban locations in US., Europe, and Asia before making our conclusion. It should also be noted that Positive Matrix Factorization (PMF) or the work by Garg and Sinha [2017] is in general applied to particulate matter. However, we have now provided correlation plots in the supplementary material.

With regards to the ration analysis using NOy species, the NOy data was not corrected as part of this study.

Section 3.5.2: Why are wind rose plotted for separate wind directions? It is very confusing. Authors should show a wind rose showing the fraction of wind coming from all the directions for O3 concentrations higher than 100 ppb. Higher fraction of wind from a particular direction would automatically point out major contribution from a particular wind direction. A polar plot with wind speed as radius axis, wind direction as angle and markers coloured according to observed O3 concentration could also be an alternative plot. How does the wind rose look like for periods with O3 concentration less than 100 ppb? If it is different from the ones for higher concentration, this would make the conclusion of higher ozone production from a particular wind direction stronger.

Authors’ response: Thank you. The wind rose plots were created from wind speeds and wind directions (blowing from), during O3 episodes ([O3]hourly > 100 ppb). The wind rose plots were analyzed and, then, classified the into 3 groups, according to the predominant local wind directions, including northerly, westerly and southerly winds. These wind roses were not plotted based on wind directions alone. However, we have now provided new plots of wind speed, wind direction (blowing from) versus the concentrations of O3, during O3 episodes and non-episodes, in the modified manuscript. Generally, high O3 concentrations relate with low wind speed (lower than 4 ms\(^{-1}\)) and relate with the predominant wind directions, especially, at 3T, 10T, 19T, 20T, 22T, 52T and 61T monitoring stations. Elevated O3 concentrations associated with northerly winds were at 22T monitoring station. At 3T, 10T, 19T, 20T and 61T monitoring stations, high concentrations of O3 associated with southerly winds. At 52T monitoring station, high concentrations of O3 associated with westerly winds. Moreover, the limited back trajectory analysis (based on NOAA HYSPLIT model) corroborates these findings and are now discussed in the manuscript.

Section 3.6: Authors need to describe the calculation of air quality index. If they have used the simple hourly average O3 concentration for calculate of AQI, then it is wrong. For calculation of hourly air quality index, O3 concentration for a give hour should be taken as the average for the previous 4 hours, current hour and next 3 hours. However, it is recommended to consider 8-hour AQI as mentioned previously in the review.
Authors’ response: Thank you. To calculate AQI for O$_3$, we calculate midpoints of 8-hour average of O$_3$ concentration from the average of hourly O$_3$ concentration of the previous four hours, at the given hour and the following three hours (this analysis is similar to the reviewer’s suggestion). To get a valid calculation, at least 6 of 8 records (75%), are needed. Then we compared the calculated midpoints with the AQI table. However, we have now included this information in the supplement material.


Technical comments:
Page 1 Line 27 – page 2 line 2; Page 2, lines 11-16: These are better suited for site description.
Authors’ response: Thank you. We have moved the information to “Section 1.2 Study Area”.

Page 2, line 17: NO is Nitric oxide and not nitrogen oxide. Nitrogen oxides refer to the family of oxides of nitrogen.
Authors’ response: Thank you. This typographical error is now corrected.

Page 2, Line 20: What is the basis of the statement “Moreover, BMR experiences primarily O3 exceedances amongst all the other gaseous criteria pollutants.”
Authors’ response: Thank you. The current study provides the basis for this statement.

Page 4, Line 4: Figure 1 should be mentioned earlier in the section.
Authors’ response: Thank you. We have now mentioned the figure earlier in the section.

Page 4, Line 20: What are the “equivalent instruments”?
Authors’ response: Thank you. The US EPA provides on its website (https://archive.epa.gov/emap/archive-emap/web/html/qa_terms.html) clarity to equivalent method. Often it may also be referred to as Alternate method which is any body of procedures and techniques of sample collection and/or analysis for a characteristic of interest which is not a reference or approved equivalent method but which has been demonstrated in specific cases to produce results comparable to those obtained from a reference method.

Page 5, Line 3: Is the measurement period 2012-2014 or 2010-2014?
Authors’ response: Thank you. This was a typographical error, which has now corrected.

Page 5, Line 7: What is the hourly “standard”?

Authors’ response: Thank you. The National Ambient Air Quality Standards of Thailand provides hourly and 8-hour average standards of CO (30 ppm and 9 ppm, respectively), hourly and annually average standards of NO2 (0.17 ppm and 0.03 ppm, respectively), hourly, 24-hour and annually average standards of SO2 (0.3 ppm, 0.12 ppm and 0.04 ppm, respectively), and hourly and 8-hour average standards of O3 (0.10 ppm and 0.07 ppm, respectively).

Page 6, line 5: Authors mention “VOCs concentrations were measured periodically only at one monitoring station limiting its usefulness as part of this study”. However, Zhang et al. [2002] have reported CH4 and NMVOC data from 10 out of 13 monitoring stations from BMR. Did the stations stopped monitoring CH4 and NMVOCs?

Authors’ response: Thank you. We provided the limitation in the manuscript “While NOx 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”.

Page 6, Line 12 and Figure 3: What is the explanation for a rather flat diel profile of NO2 at roadside sites. Roadside sites are influenced maximum by traffic emissions, and one would expect a bimodal shape of diel profile.

Authors’ response: Thank you. We have now included the explanation in the manuscript.

Page 8: The rate constants and photolysis frequencies should be expressed in cm³ molecule⁻¹ s⁻¹ and s⁻¹ respectively.

Authors’ response: Thank you. We calculated j₁ and k₃ in the unit of s⁻¹ and ppm⁻¹ min⁻¹, since we wanted to compare our values with other published studies that they reported their values in min⁻¹ and ppm⁻¹ min⁻¹ (Clapp and Jenkin, 2001), (Tiwari et al., 2015).

Tiwari, S., Dahiya, A., and Kumar, N.: Investigation into relationships among NO, NO2, NOx, O3, and CO at an urban background site in Delhi, India, Atmospheric Research, 157, 119-126, doi:10.1016/j.atmosres.2015.01.008, 2015.


However, we have now provided j₁ and k₃ in the unit of s⁻¹ and cm³ molecule⁻¹ s⁻¹ in the supplement material.

Page 9, line 9: The titration of O3 with NO will not effectively reduce the O3 concentrations.

Such a titration process with produce NO2 which will again photolyze in the daytime and produce O3.
Authors’ response: Thank you, however, we believe that the titration of O₃ by fresh NO emitted from vehicles probably causes the lower O₃ concentration observed at the roadside sites. Several studies reported the similar results, for example, Chan et al., (1998) studied surface ozone pattern in Hong Kong and reported that “In fact, this O₃ sink is a common feature observed in many countries in the Northern Hemisphere, such as in Great Britain and Canada. In these two countries, the urban stations in central London (Bower et al. 1989; UKPORG 1990) and Alberta (Angle and Sandhu 1988) show lower O₃ concentrations than their counterparts in the rural areas. This can be explained by the fact that the fresh precursor emissions from traffic and other sources cause direct chemical scavenging of O₃.” And “Indeed, Bell et al. (1970, 1977) has shown that even under light wind conditions, pollutants generated from local sources will be dispersed within 2–3 h. Thus, the titration effect of the fresh O₃ precursors, especially NO, emitted from the metropolitan area of Hong Kong leads to the lower O₃ levels in the urban stations in our study.” Ghim and Chang (2002) studied ground-level ozone distribution in Korea and reported that “many studies reveal that background ozone concentrations in the Northern Hemisphere are around 3 5-40 ppb [Akimoto et al., 1996; Husar, 1998]. However, even in summer, monthly mean ozone levels in Korea are lower than this background level. This could be primarily due to local effects of titration of O₃ by fresh NOx emissions, since most ozone monitoring stations are located in or near major cities [Fuentes and Dann, 1994]”. Munir et al., (2014) studied the diurnal variations of O₃ in the UK and reported that “the lowest ozone concentrations are exhibited by Marylebone monitoring site which is located approximately 1 m from the edge of Marylebone road. This road has six lanes and has a flow of 80,000 vehicles per day. Most probably titration of ozone by fresh NO emitted by road transport keeps ozone concentrations low at this site.”


Page 12, line 2: Please check the lifetime of O₃. It should be few days (if not few weeks) in urban atmosphere.

Authors’ response: Thank you. The lifetime of O₃ that was provided in our manuscript was the lifetime in “a polluted urban atmosphere” where the lifetime of O₃ is relatively short in this atmospheric condition. Monks et al., (2015) that reported “....ozone has a relatively short atmospheric lifetime, typically hours, in polluted urban regions where concentrations of its precursors are high, its lifetime in the free troposphere is of the order of several weeks (Stevenson et al., 2006; Young et al., 2013)...”


Page 12, Line 15 - Page 12, Line 5: Such description is better suited for introduction.
Authors’ response: Thank you. We have now modified the manuscript by moving this description to the introduction section.

Page 13 Line 18 to page 19 line 2: Such discussion is well suited for outlook after proper restructuring.
Authors’ response: Thank you. Based on the reviewer, we have now modified our manuscript.

Figure 1: I would recommend showing airmass back trajectories rather than showing wind directions with two indicator arrows.
Authors’ response: Thank you. Based on the reviewer, we have now modified the figure and included the airmass back trajectories based on NOAA HYSPLIT model.

Figure 2: Ambient variability should also be shown along with average values. Authors should also show the concentrations of NO, in addition to CO, SO₂, O₃, and NO₂. The colour for year 2010 and 2011 look same in panel “e”.
Authors’ response: Thank you. We did not provide a plot of NO in the manuscript, since this species is not a criteria pollutant. However, we have added a plot of the concentrations of NO and modified the figure in the modified manuscript.

Figure 3: Quality of figure should be improved (overall presentation, axis labels and legends). Ambient variability (as interquartile range or 1 _ standard deviation) should also be shown in addition to the average values. This should be done for other figures also in the paper.
Authors’ response: Thank you. We have now modified the figure by adding standard deviations, and improved axis labels, and legends.

Figure 6: The minimum wind speed bin should be 0.5 – 2.0 (not 201). Please use the same radius scale for the wind rose plots.
Authors’ response: Thank you. We have provided a new figure in the modified manuscript.

Table 1: Please refer to the comment for section 3.3.
Authors’ response: Thank you. We have now modified our manuscript based on the reviewer’s suggestion.
Table 3: Authors should also include the SO₂/NOₓ ratio reported from various cities in India for mobile sources as reported by Mallik and Lal, 2014.


Authors’ response: Thank you. We have now included the SO₂/NOₓ ratios from the study of Mallik and Lal, 2014 in the manuscript.

Reviewer #2

We wish to thank the reviewer for the careful and thoughtful review of our manuscript. We appreciate the reviewer’s comments “Overall, the article is well written and examines the interaction of Ozone with NOₓ regime. The analysis was well done.”

All the comments and suggestions are now incorporated in the manuscript.

Line 12: the statement is made, "On average, the number of hourly O₃ exceedences ranged from 1 - 60 hours a year." This line is confusing. The overall average should be a value, not a range. If you wish to express it as a range, then do it by year, such as 2010 that average was XX hours, 2011, the average was XX hours. This range of 1-60 hours makes no sense.

Authors’ response: Thank you. We have now incorporated the change in the modified manuscript.

Section 2, Methodology line 12: When you express a range (this applies throughout, do not mix the units and values. In Section 2, Methodology line 12 you state the temperature is (~35C - 40C). This appears to read that it ranges from 35 degrees to - (minus) 40 degrees. Do this instead: (35 - 40 C).

Authors’ response: Thank you. We have now incorporated the change in the modified manuscript.

Section 2, Methodology line 21: it states, " It is assumed that the monitoring sites used were representative of BMR specific patterns and trends." I think it goes without stating this that the professionals at the PCD would have done this and this does not need to be stated, but you would hope you would infer this. Remove this statement.

Authors’ response: Thank you. We have now incorporated the change in the modified manuscript and the statement has been removed.

Section 2, Methodology, line 27 -29: you list the sites (19T, 20T, etc...) which mean absolutely nothing to the reader then you state in line 29 that the figure shows these. The statement that
mentions the figure should be the first line to the paragraph, not the last line. Move this line to the front so the reader can go get the figure look at it while you read the information.

Authors’ response: Thank you. We have now modified the manuscript by removing site lists and referring the figure earlier in the section.

Section 2.2, line 2: you mention wind speed and direction. Is this average or vector data? Please state. This is important when calculating direction from which winds are blowing.

Authors’ response: Thank you. The wind speed and wind direction are hourly averages.

Section 2.2, line 10: it is mentioned that equipment and monitoring station are calibrated every year. This is vague and could cast a shadow on validity of data. does this mean that this is done only once per year? Pollution instruments and met, or only met instruments. I am sure the PCD does calibrations more often than once annually. Please clarify this statement.

Authors’ response: Thank you. As indicated in the manuscript, the data were collected, and after QA/QC, were provided to us by the Pollution Control Department (PCD), Thailand. Data loggers are calibrated/checked at least every 15 days. Air inlets are cleaned at least every 15 days. Equipment is single-point calibrated and multi-point calibrated at least every 15 days and at least every 3 months. Monitoring stations and equipment are audited by external auditors every year. We have modified our manuscript to make a clarification.

Section 3.3 line 24: you use the term "atmospheric boundary layer." Is this the same as planetary boundary layer that was used previously? If it is the same term, then be consistent. If it isn’t then please explain what this term means on how it differs from the PBL.

Authors’ response: Thank you. We have now corrected the manuscript by using “planetary boundary layer” instead of “atmospheric boundary layer” to provide consistency in the manuscript.

Page 8, line 11: Please explain why the ratios of NO$_2$ and NO show significant difference. You make the statement but you don’t say why. this is an important claim that you make in this paper.

Authors’ response: Thank you. As suggested by the reviewer, we have now removed this from our manuscript.

Page 9, line 9: you state, "In conclusion, the titration of O$_3$ and NO is perhaps one of the most important processes..." Please elaborate about why this is so important.

Authors’ response: Thank you. The titration of O$_3$ by NO is perhaps one of the most important processes to reduce O$_3$ concentration at roadside sites, due to this monitoring station type is more affected by fresh NO emitted from vehicles than the other monitoring station types. Several studies reported the effect of the titration of O$_3$ by NO, for example, Chan et al., (1998) studied surface ozone pattern in Hong Kong and reported that “In fact, this O$_3$ sink is a common feature observed
in many countries in the Northern Hemisphere, such as in Great Britain and Canada. In these two countries, the urban stations in central London (Bower et al. 1989; UKPORc 1990) and Alberta (Angle and Sandhu 1988) show lower O₃ concentrations than their counterparts in the rural areas. This can be explained by the fact that the fresh precursor emissions from traffic and other sources cause direct chemical scavenging of O₃.” And “Indeed, Bell et al. (1970, 1977) has shown that even under light wind conditions, pollutants generated from local sources will be dispersed within 2–3 h. Thus, the titration effect of the fresh O₃ precursors, especially NO, emitted from the metropolitan area of Hong Kong leads to the lower O₃ levels in the urban stations in our study.” Ghim and Chang (2002) studied ground-level ozone distribution in Korea and reported that “many studies reveal that background ozone concentrations in the Northern Hemisphere are around 35-40 ppb [Akimoto et al., 1996; Husar, 1998]. However, even in summer, monthly mean ozone levels in Korea are lower than this background level....This could be primarily due to local effects of titration of O₃ by fresh NOx emissions, since most ozone monitoring stations are located in or near major cities [Fuentes and Dann, 1994]”. Munir et al., (2014) studied the diurnal variations of O₃ in the UK and reported that “the lowest ozone concentrations are exhibited by Marylebone monitoring site which is located approximately 1 m from the edge of Marylebone road. This road has six lanes and has a flow of 80,000 vehicles per day. Most probably titration of ozone by fresh NO emitted by road transport keeps ozone concentrations low at this site.”


However, we have removed this from the manuscript.

Page 11, line 5: you state, “However, a negative delta O₃ may be negative. However, it appears that the data doesn’t support this in the paragraph. Why is this statement made?

Authors’ response: Thank you. We put this statement to clarify that a negative delta O₃ was possibly to be observed due to O₃ deposition and/or O₃ consummation. Our analysis, negative values of delta O₃ were observed several times, however, the average of those was positive.
Assessment of Air Pollution Gaseous Pollutants in Bangkok Metropolitan Region, Thailand

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Abstract. Analysis of gaseous criteria pollutants in Bangkok Metropolitan Region (BMR), Thailand, during 2010–2014 reveals that while the hourly concentrations of CO, SO2 and NO2 were mostly below the National Ambient Air Quality Standards (NAAQs) of Thailand. However, the hourly concentrations of O3 frequently exceeded the Thailand NAAQs standard. The maximum concentration results reveal that the problem of high O3 ranged from 120–190 ppb. On average, the number of hourly O3 exceedances ranged from 1–60 hours a year depending on monitoring station locations. The exceedances occurred during the summer and winter, dry seasons, concentration continuously persisted in this area. Interconversion between O3, NO and NO2 indicates crossover points between the species occur when the concentration of NOx ([NOx] = ([NO]+[NO2])) is ~60 ppb. However, when [Under low NOx regime ([NOx] < 60 ppb), O3 is the dominant species; conversely, while, under high NOx regime ([NOx] > 60 ppb), NO dominates when [NOx] > 60 ppb. The calculated photochemical reaction rate (the reaction between NO2 with sunlight), during photostationary state ranges from 0.12 to 1.22 min⁻¹. Linear regression analysis between the concentrations of Ox ([Ox] = ([O3]+[NO2])) and NOx provides the role of local and regional contributions to Ox. Both During O3 episodes ([O3]hourly > 100 ppb), the values of the local and regional Ox contributions enhance the concentration were nearly double of Ox. Values of the local and regional Ox contributions during non-episode were ~14.54 ppb and ~0.13[NOx] to 0.33[NOx], respectively. Those values were about double during O3 episodes ([O3] > 100 ppb)-episodes. Ratio analysis suggests that the major contributors of primary pollutants over BMR are mobile sources (CO:NOx = 19.8). The Air Quality Index (AQI) for BMR was predominantly between good to moderate. Unhealthy, 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, 2018a). A majority of the country’s development has occurred within and around Bangkok (BKK), located at (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 (O₃) (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 O₃ during the previous day, in elderly patients (≥ 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 O₃ in Thailand were reported in several studies. Long-range transport played an important role in increasing O₃ concentration in Thailand. Generally, long-range transports from the Asia continental contained higher O₃ 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 O₃ concentrations and seasonal fluctuations of O₃, respectively (Zhang and Oahn, 2002). In suburban areas of BKK, volatile organic compounds (VOCs) tended to be a potential factor to enhance O₃ 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 NOₓ, 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 stations, 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

Bangkok (BKK), the capital city of Thailand, has the largest population and population density in Thailand. Bangkok Metropolitan Region (BMR) refers to Bangkok and the five adjacent provinces, including Nakhon Pathom, Pathum Thani, Nonthaburi, Samut Prakan, and Samut Sakhon. These five provinces are closely linked to BKK in terms of traffic and industrial development (Zhang and Oanh, 2002). Since 1995, BKK has experienced exceedances in Thailand National Ambient Air Quality Standard (NAAQS) for particulate matter (PM) and ozone (O$_3$) (PCD, 2015). The largest number of O$_3$ exceedances ([O$_3$]$_{hourly}$ > 100 ppb) occurred in the year 2000 with 174 hours of exceedances (Oanh and Zhang, 2004). Furthermore, BMR is considered as a region with the worst air quality in Thailand (Watcharavitoon et al., 2013). The transportation and industrial sectors are considered to be the major sources of air pollutants in BKK (Watcharavitoon et al., 2013). The number of vehicles in Thailand has increased since 1989. During 2014, about 36 million new vehicles were registered 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% is Compressed Natural Gas (CNG). According to the database of the
Department of Industrial Work (DIW), Thailand, the number of registered manufacturing plants in Nakhon Pathom, Pathum Thani, Nonthaburi, Samut Prakan, and Samut Sakhon are 3,282 (DIW, 2016), 3,756 (DIW, 2016a), 1,981 (DIW, 2016b), 7,357 (DIW, 2016c) and 6,035 (DIW, 2016d). A variety of manufacturing facilities are located on the outskirts of BKK, including, metal, auto parts, paper, plastic, food, chemical manufacturing and power plants.

In this study, gaseous criteria pollutants including carbon monoxide (CO), nitrogen oxide (NO), nitrogen dioxide (NO₂), sulfur dioxide (SO₂) and O₃ concentrations and trends in BMR during 2010-2014 are investigated. O₃ and its precursors (only NO and NO₂) are analyzed since they are the species that were measured at a majority of the monitoring sites. Moreover, BMR experiences primarily O₃ exceedances amongst all the other gaseous criteria pollutants. Interconversion between O₃ and its precursors and photochemical reaction rate during photostationary state are examined to assess O₃ formation over BMR. Local emission, regional contribution and possible emission sources of pollutants that associate with O₃ formation are identified.

2. Methodology

1.2 Study Area

BKK is located at latitude and longitude of 13°45' N and 100°85' E, over the low-flat plain of Chao Praya River, elevation height ~2.3 m above mean sea level. Thailand has three official seasons—local summer (around February- to May), rainy (around May- to October) and local winter (around 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. Around October- to April, this region is influenced by Northeast monsoon wind that travels from the northeastern and the northern parts of Asia (China and Mongolia). This monsoon wind brings a cold and dry air mass, resulting in dry season (local summer and local winter) in Thailand. The dry season in Thailand can be classified into two minor local seasons—winter and summer. The local winter in Thailand is characterized by cool and dry
weather, while the local summer is characterized by hot (~35 \degree C to 40 \degree C) to extremely hot weather (> 40.0 \degree C) due to the strong solar radiation. During the dry season, storms may occur especially during the seasonal transition (TMD, 2015). Due to its location in the coastal area of the Gulf of Thailand, land and sea breezes may play an important role on pollution dispersion over BMR. Phan and Manomaiphiboon (2012) showed that sea breezes from the Gulf of Thailand frequently occur during winter. Strong sea breezes that penetrated inland 22-55 km were found during the early to mid afternoon.

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. Hourly observations collected by Pollution Control Department (PCD), Thailand, from 15 monitoring sites located in BMR are analyzed in this study. It is assumed that the monitoring sites used were representative of BMR-specific patterns and trends. The monitoring sites are categorized into three categories: Bangkok (BKK) sites, Roadside sites, and BKK suburb sites. Seven Bangkok sites including 3T, 5T, 10T, 11T, 12T, 15T and 61T sites, refer to the air quality monitoring sites that are located within BKK’s residential, commercial, industrial and mixed areas. These monitoring sites are ~50-100 m away from the road. Two roadside sites including 52T and 54T sites, refer to the monitoring sites that are located in BKK within 2-5 m from the road (Zhang and Oanh, 2002). Six BKK suburb sites including 13T, 14T, 19T, 20T, 22T and 27T sites, refer to the monitoring sites that are located in provinces adjacent to BKK (Pathum Thani (site 20T), Nonthaburi (sites 13T and 22T), Samut Prakan (site 19T), and Samut Sakhon (sites 14T and 27T)). Figure 1 shows a map of BMR with the major monsoon winds over this region and the monitoring sites’ location.

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

The data sets in this study were provided by the PCD. 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 species pollutants and meteorological parameters including wind speed (WS), wind direction (WD), temperature (T) and relative humidity (RH) were automatically collected with auto calibration at the monitoring stations. Manual quality control was performed when unusual observations were found. The external audit of the equipment and monitoring stations were calibrated every year. Data availability is provided in Figure 1, 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 NO₂ were measured using chemiluminescence detection (Thermo Scientific 42i). SO₂ was measured using ultraviolet (UV) fluorescence detection (Thermo Scientific 43i) and O₃ 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 (Watchavitoon et al., 2013). All the meteorological measurements were made by Met One or equivalent instruments.

Data analysis, statistical analysis (t-test) and plots are performed using Excel 2016. Predominant wind directions over BMR are illustrated by wind rose diagrams which related to O₃ concentrations are performed using WRPLOT, Openair package (tool for the analysis of air pollution data) on RStudio program (free software from Lake Environmental).
3. Result and Discussion

3.1 Status of Pollution in BMR during 2010- to 2014

The Figure 2 a) to e) shows the maximum and average concentration of gaseous criteria pollutants, during 2012-2010 to 2014, from the 15 monitoring sites, were analyzed and 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) as shown in (PCD, 2018)). Since, NO is not a criteria pollutant, only the maximum and average concentrations are presented (Fig. 2(a)-(d)). During the 5 years of the study period, the maximum hourly concentrations of CO, NO2 and SO2 were mostly lower than their hourly standard 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±0.21 ppm over roadside sites and ~0.7±0.4 ppm over BKK sites, ~60.5±42.7 ppb, and ~30.9±8.1 ppb, respectively. Elevated SO2 were commonly observed at BKK suburb sites. The hourly maximum concentrations of CO ranged from ~3-8 ppm. than other sites. The average concentrations of NO2, SO2 at BKK suburb sites were ~32.2±17.7 ppb, 21.1±13.6 ppb and 16.3±11.9 ppb over 4.0±2.3 ppb. The average concentrations of O3 during daytime (6:00 to 18:00 LT) over BKK sites, roadside sites, BKK sites and BKK suburb sites, respectively. The hourly maximum concentrations of NO2 ranged from 62-180 ppb (an exceedance was found at 52T monitoring station, during 2013). High SO2 concentrations were frequently found over BKK suburb sites. The average concentrations of NO2, SO2 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±3.9 ppb, 3.0±2.1 ppb and 2.6±2.3 ppb over ~9.1±4.9 ppb and ~14.2±5.4 ppb, respectively. The 24-hour average O3 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\textsubscript{2} and SO\textsubscript{2} decreased or remained constant, the concentration of O\textsubscript{3} tended to increase during the study period (Figure III, supplement material).

An O\textsubscript{3} exceedance was recorded when an hourly concentration of O\textsubscript{3} was greater than 100 ppb (hourly O\textsubscript{3} standard). Figure 2 f) to g) illustrate the number of hourly O\textsubscript{3} exceedances, which they are shown by locations and by seasons, respectively. The hourly maximum concentration of SO\textsubscript{2} ranged from 13-163 ppb. O\textsubscript{3} exceedances at BKK suburb sites were more frequently observed than those at the other sites. The average number of hourly O\textsubscript{3} exceedances was \~16 hours year\textsuperscript{-1} at BKK sites, \~9 hours year\textsuperscript{-1} at roadside sites and \~43 hours year\textsuperscript{-1} at BKK suburb sites. The hourly O\textsubscript{3} exceedances were commonly observed during dry season than during the transitional period between the seasons (May) and rarely observed during wet season.

Even though the hourly maximum concentrations of the other gaseous species were generally lower than their standards, the hourly maximum concentrations of O\textsubscript{3} were greater than its standard. The average concentrations of O\textsubscript{3} were \~22.0±19.8 ppb, 17.9±16.9 ppb and 13.3±12.7 ppb over BKK suburb sites, BKK sites and roadside sites, respectively. The hourly maximum concentration of O\textsubscript{3} ranged from 68-190 ppb. O\textsubscript{3} exceedances at BKK suburb sites were more frequently occurred than those at other sites. The average number of hourly O\textsubscript{3} exceedances during 2010-2014 for BKK suburb sites, BKK sites and roadside sites ranged from \~43±21 hours a year, \~16±9 hours a year, and \~9 hours a year (Fig. 2(e)). Moreover, the exceedances of O\textsubscript{3} concentration were commonly found during the dry season, especially in January (winter). During May, the transitional period between wet and dry seasons, the number of O\textsubscript{3} exceedances decreased and O\textsubscript{3} exceedance rarely occurred during wet season (Fig. 2(f)).

### 3.2 Diurnal Variation of the Gaseous Species

The primary precursors for tropospheric O\textsubscript{3} in the urban environment, are oxide of nitrogen (NO\textsubscript{x}; refers to NO + NO\textsubscript{2}) and non-methane volatile organic compounds (VOCs), methane or CO (The Royal Society, 2008, Monks et al., 2009; Cooper et al., 2014). NO\textsubscript{x} was measured continuously at all the monitoring sites. However, VOCs concentrations were measured periodically only at one monitoring station limiting its usefulness as part of this study.

Diurnal variations of O\textsubscript{3} and its precursors over BMR during 2010-2014\textsuperscript{gaseous pollutant} are shown in Figure (3(a) to (c)). The diurnal variations of O\textsubscript{3} show a typical single-peak...
pattern (Aneja et al., 2001) with the concentrations increased after sunrise and reached the peak around 15:00 local time (LT). The concentrations begin to decline in the evening and reach the minimum concentrations around 7:00 LT in the next morning. The concentrations of $O_3$ at the peaks of the diurnal variations of $O_3$ were ~40 ppb over BKK sites, ~30 ppb over roadside sites and ~45 ppb over BKK suburb sites. The diurnal variations of NO and NO$_2$ show double-peak patterns—a bimodal pattern with the concentrations increase around 5:00 LT and reach the first-peak around 7:00-9:00 LT before they decline. The concentrations of NO and NO$_2$ start rising and reach the first-peak around ~7:00 to 9:00 LT and ~21:00 to 22:00 LT, respectively. The NO-concentrations of NO at the morning-first- and the second-peak were ~40 ppb and ~23 ppb at BKK sites, ~110 ppb and ~73 ppb at roadside sites and BKK suburb sites were ~40 ppb, 110 ppb and ~30 ppb. In the afternoon they were ~23 ppb, 73 ppb and ~13 ppb at BKK suburb sites. The NO$_2$-concentrations of NO$_2$ at the morning-first- and the second-peak over BKK and BKK suburb sites were ~23 ppb and 20 ppb and those at the afternoon peak were ~28 ppb at BKK sites, ~33 ppb and 22-37 ppb. The NO$_2$-concentrations over at roadside sites ranged from ~22-37 ppb and were near constant during the day, and ~20 ppb and ~22 ppb at BKK suburb sites. Even the diurnal variations of NO$_2$ show a bimodal pattern at roadside sites, the pattern was flatter than at other sites. The flatter pattern of NO$_2$ at roadside sites reveals that this monitoring station type was affected by high concentration of NO$_2$ all day. The diurnal variations of CO show double-peak patterns—a bimodal pattern with the first- and the second-peak occur around ~8:00 LT and 21:00 LT. The diurnal variations of CO are similar to those of NO, respectively. The concentrations increase around 4:00-5:00 LT and reach the first-peak around 7:00-8:00 LT before they decline. The CO-concentrations start rising and reach the second-peak at night. The CO concentrations at the morning peak were ~1 ppm, 2 ppm and 1 ppm and those at the night peak were ~1 ppm, 1.5 ppm and 1 ppm, over) at BKK sites, ~2 and ~1.5 ppm at roadside sites, and ~1 ppm (both peaks) at BKK suburb sites, respectively.

Diurnal patterns. The first peak of the diurnal variations of NO, NO$_2$, and CO correspond to road traffic patterns and similar to those in other big cities (Tiwari et al., 2015). The study of Leong et al. (2002) on air pollution measurement in BKK showed that, in BKK, morning rush hour occurred during 7:00-9:00 LT and evening rush hour occurred during 16:00-18:00 LT. During traffic rush hours, traffic volume was high with low vehicle speeds. While the first
peak of the diurnal pattern of pollutants occurred during the morning traffic rush hour, the). The second peak of those occurred ~3- to 5 hours after the evening traffic rush hour. This is (16:00 to 18:00 LT) (Leong et al., 2002), due to a combination of pollutants emissions and collapse of the planetary boundary layer during this time. The evening planetary boundary layer is characterized by weak turbulence and diffusion, allowing pollutants to accumulate in the layer (Arya, 1999; Jacobson, 2012).

The concentrations during this time. The diurnal variations of SO2 show a bimodal pattern with the first- and the second-peak of SO2 start increasing around 5:00 LT and reach maximum around 8:00 LT before the decline occurred ~8:00 LT and 21:00 LT, respectively. The concentrations of SO2 at the morning first- and the second-peak were ~3 ppb over (both peaks) at BKK sites and ~3 ppb (both peaks) at roadside sites, and ~6 ppb over BKK suburb sites. The concentrations of SO2 increase again in the afternoon and reach a second peak around 21:00 LT over roadside site. Over BKK sites and BKK suburb sites, the concentrations of SO2 are nearly constant after 19:00 LT. The concentrations of SO2 at the second peak over roadside sites were ~2 ppb and ~3-4 ppb over BKK sites and at BKK suburb sites. The double-peak pattern of SO2 over At the roadside sites, the peaks are more obvious than the other sites. The result indicates that at this monitoring station type, SO2 is primarily influenced by emission primarily emissions from vehicle exhaust using high sulfur content fuel, especially high sulfur diesel. The study of ambient air SO2 patterns in European cities by (Henschel et al. (2013)) showed that diurnal patterns of SO2 had a double-peak pattern which the morning peaks more likely related to emission during rush hour, evening peaks were possibly caused by traffic and meteorology—collapse of the planetary boundary layer). It is noteworthy that BKK has a large diesel engine fleet (an estimated 25 % of registered vehicles) (DLT, 2015a-2015). The diesel fuel contains ~0.035 %wt Sulphur (DOEB, 2017). Given the timing of SO2 peak (morning automotive rush hour), it is likely that SO2 is emitted by automotive diesel engine exhaust. 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 O3 concentration (Δ[O3]/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 O3 concentration characteristics). The diurnal variations of Δ[O3]/dt is a combination of O3 chemistry and meteorology. In general, Δ[O3]/dt during wet season were
lower than those during dry season. However, during local winter, the rates of change in O3 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 O3 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 O3 is inhibited and the planetary boundary layer becomes more stable resulting in O3 reduction through chemical reactions (for example, the oxidation of O3 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 O3, NO and NO2—and Photochemical Reaction

The primary precursors for tropospheric O3 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 all the chemical reactions for O3 formation during 10:00 to 16:00 LT. This time window is chosen due to the fully developed atmospheric planetary boundary layer with well-mixed condition (Pochanart et al., 2001) in order to avoid accumulation due to 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. Analysis and calculation are performed only during dry season.

The relationship among three chemical species (NO, NO\(_2\) and O3) under PSS is presented by Eq. (1) (Seinfeld and Pandis, 1998)

\[
[O_3]_{PSS} = \frac{j_1[NO_2]}{k_3[NO]} 
\]

Eq. (1)

Where \([O_3]_{PSS}\) is the concentration of O3, 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 O₃, respectively. According to Eq. (1), the concentration of O₃ depends on the ratio of NO₂ and NO. Therefore, other chemical reactions or processes that affect NO₂ and NO species will also affect O₃ concentrations in the atmosphere (Jacobson, 2012).

The ratio of NO₂ and NO are calculated only during dry season. During dry season, the values of the ratios range from 0.54-4.33 in winter and from 0.87-4.33 in summer. T-test values for the ratios exhibit no significant difference with season (P-value > 0.05). While there is no significant difference with season, the t-test values exhibit a significant difference with locations of monitoring sites. The ratios of NO₂ and NO show significantly different between roadside sites and non-roadside sites (BKK sites and BKK suburb sites) with P-value < 0.05.

In this study, \( j_1 \) is calculated based on Eq. (1), since we cannot directly measure it. The values of \( j_1 \) range from 0. The values for \( k_3 \) (ppm⁻¹ min⁻¹) is calculated by Eq. (2) (Seinfeld and Pandis, 1998; Tiwari et al., 2015).

\[
k_3 = 3.23 \times 10^3 \exp[-1430/T]
\]  \hspace{2cm} \text{Eq. (2)}

During dry season, the values of \( j_1 \) and \( k_3 \) ranged from 0.12 to 1.22 min⁻¹ in winter and from 0.13-0.90 min⁻¹ in summer (Table (and 28.3 to 30.9 ppm⁻¹)). T-test values for \( j_1 \) exhibit no significant difference with season and location (P-value > 0.05), min⁻¹, respectively. The ratio of [NO₂] 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 cm³ molecule⁻¹ s⁻¹) at the three monitoring station types are provided in Table II, supplement material.

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

\[
k_3 = 3.23 \times 10^3 \exp[-1430/T]
\]  \hspace{2cm} \text{(2)}

During dry season, Figure 5 a) to c) shows the values of \( k_3 \) range from 28.3-29.8 ppm⁻¹ min⁻¹ in winter, relationships between NO, NO₂ and O₃, their crossover points, and from 30.0-30.9 ppm⁻¹ min⁻¹ in summer. T-test values for \( k_3 \) exhibit a significant difference with season (P-value < 0.05) and no significant difference with locations of the monitoring sites (P-value > 0.05) (Table (1)).
Since $k_2$ is a function of temperature ($T$), therefore, the maximum values of $k_2$(29.6 and 30.8 ppm\textsuperscript{-1} min\textsuperscript{-1} in winter and summer, respectively) occur during the afternoon (around 15:00 LT) when the temperature is highest. The maximum values of $k_2$ from this study conforms to the $k_2$ value (29.3 ppm\textsuperscript{-1} min\textsuperscript{-1}) that was found at an urban background site in Delhi, India, which the peak occurred at 15:00 LT (Tiwari et al., 2015).

Due to high value of $j_1$, high O\textsubscript{3} concentrations are expected to be found at 11T, 20T and 52T sites. However, high O\textsubscript{3} concentrations were found only at 20T and 52T sites, but low at 11T site. The low level of O\textsubscript{3} concentration at 11T site has an association with the titration of O\textsubscript{3} by NO, since high NO concentrations were observed at 11T site. In conclusion, the titration of O\textsubscript{3} by NO is perhaps one of the more important processes that control O\textsubscript{3} concentrations in urban areas.

To gain a better understanding of O\textsubscript{3} and its precursors over BM, the concentrations of NO, NO\textsubscript{2} and O\textsubscript{3} are plotted against the concentrations of NO\textsubscript{x}. Polynomial trend lines are added in order to investigate the interconversion among these species. Figure (4(a)-(c)) show relationship and crossover points between the species distributions. The crossover points occur when the concentration of NO\textsubscript{x} is ~60 ppb. At this point, two regimes are identified, including low NO\textsubscript{x} regime and high NO\textsubscript{x} regime. Under the low NO\textsubscript{x} regime ([NO\textsubscript{x}] < 60 ppb), O\textsubscript{3} is the dominant species among the others, and NO\textsubscript{2} concentrations are higher than NO for NO\textsubscript{x} species. Conversely, under the high NO\textsubscript{x} regime ([NO\textsubscript{x}] > 60 ppb), NO and NO\textsubscript{2} increase and, the concentrations of O\textsubscript{3} rapidly decrease. Under the high NO\textsubscript{x} regime, the decreased declination of O\textsubscript{3} trend-lines may describe O\textsubscript{3} removal process through the titration of O\textsubscript{3} by NO.

### 3.4 Local and Regional Contribution to O\textsubscript{x}

The O\textsubscript{x} concentration is the summation of O\textsubscript{3} and NO\textsubscript{2} concentration. Under the PSS condition, concentration of NO, NO\textsubscript{2} and O\textsubscript{3} approach an equilibrium and the concentration of O\textsubscript{x} may be considered constant (Keuk et al., 2009). Since the conversion between O\textsubscript{3} and NO\textsubscript{2} in the urban and suburban atmosphere is rapid, the use of O\textsubscript{x} to represent production of oxidants is more appropriate than only using O\textsubscript{3} (Lu et al., 2010). The local or NO\textsubscript{x}-dependent contribution refers to O\textsubscript{x} concentration that is influenced by concentration of the local pollutants. The regional
contribution or NOx-independent refers to the background concentration of O\textsubscript{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 contribution of O\textsubscript{x} at the three monitoring station types. The effects of the local and regional contributions to O\textsubscript{x} concentration are analyzed by plotting O\textsubscript{x} concentrations against NO\textsubscript{x} concentrations and fitting the plot with a linear regression (y = mx + c). The concentration of NO\textsubscript{x} and O\textsubscript{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 2 shows the comparison between the fitted linear regressions from this study with other studies. The average background O\textsubscript{x} concentrations over BMR during non-episodes ([O\textsubscript{3}]\textsubscript{hourly} < 100 ppb) and episodes are([O\textsubscript{3}]\textsubscript{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. Therefore, The results reveal that elevated O\textsubscript{3} formation concentrations during the episode days were influenced by both the local and regional contributions of O\textsubscript{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\textsubscript{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. utilized hourly O\textsubscript{3} concentrations during 10:00-16:00 LT reflecting the role of photochemistry in O\textsubscript{3} formation. Thus, the difference between O\textsubscript{3} concentration measured at Samut Sakhon Provincial Administrative (site 27T) and Bangkok University Rangsit Campus (site 20T) during the predominant wind direction should reflect the difference in the amount of O\textsubscript{3} leaving and entering the city whenever the winds are out of the Southwest or Northeast direction (1989) analysed high-O\textsubscript{3} events in Atlanta, GA, and showed that rural background O\textsubscript{3} during high O\textsubscript{3} concentrations (Fig. 6). This analysis provides the net increment of photochemical O\textsubscript{3} added to an air mass over the course of the day as it advects over the city. For a more rigorous
delta O$_3$ analysis, we need to consider the role of wind speed. Lindsay et al. (1989) analyzed high O$_3$ events in Atlanta, GA, and showed that rural background O$_3$ during episode days ([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, enhancing. This enhanced the total O$_3$ concentration to 80- to 85 ppb. In our study, during the different in the concentrations of O$_3$ overat the upwind and downwind monitoring sites (20T and 27T monitoring station) are averaged during. 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 in during dry season when backward trajectories from theo 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 revealed backward trajectories revealed N-NE, S-SW wind directions with high O$_3$ concentrations ([O$_3$] > 80 ppb) at the monitoring sites. The(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. However, 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 about -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/NOₓ ratios and low SO₂/NOₓ ratios. In contrast to mobile sources, the characteristic of point sources are low CO/NOₓ ratios and high SO₂/NOₓ ratios (Parrish et al., 1991; Rasheed et al., 2014).

Table (3) shows the comparison between the CO/NOₓ and SO₂/NOₓ ratios from this study and when compared with other studies. The ratio of CO/NOₓ is 19.8 and the ratio of SO₂/NOₓ is 0.1 over BMR. This suggests that the major contributors of primary pollutants over the BMR are mobile sources. However, this region may also be influenced by manufacturing facilities’ point sources (SO₂ contributor) on the outskirts of the BKK. These point sources will impact the concentrations of SO₂, NOₓ and CO. Correlation plots among species are provided in Figure V, supplement material.

3.5.2 Effects of Pollutant Transport

In general, O₃ has a short (approximately hours) lifetime in polluted urban atmosphere. However, O₃ has a longer lifetime of several weeks in the free troposphere. This occurrence may allow O₃ to be transported over continental scales (Stevenson et al., 2006; Young et al., 2013; Monks et al., 2015). Figure 68 shows high O₃ concentrations ([O₃]hourly > 100 ppb), during episodes and non-episodes, with the predominant wind directions over BMR during 2010 to 2014 and wind speeds. The results show that O₃ exceedances are associated with the local wind directions which are related to locations of the monitoring sites. High O₃ concentrations are associated with the three low wind speed and predominant wind directions; westerly, northerly and southerly winds. Elevated O₃ concentrations were observed with wind speed lower than 4 ms⁻¹ with northerly winds were at 11T, 13T, 14T, (22T and 27T sites. At sites, southerly winds (3T, 5T, 10T, 42T, 15T, 19T, 54T, 20T and 61T, high O₃ concentrations are associated with 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 O₃ concentrations were predominantly observed with westerly wind directions. The results from this study are supported by an earlier study observed (Sahu et al., 2013a, 2013b).
3.6 Air Quality Index for O₃ Management

Enhanced ambient air pollution has an association with increased risk of adverse cardiovascular morbidity and mortality for humans. For example, increased levels of O₃ causes coughing, reduces lung function, enhances pulmonary inflammation and may increase the risk of death due to respiratory diseases (US.EPA, 2017c). While adverse health effects may occur in healthy people, enhanced ambient air pollution is a serious threat to sensitive groups (i.e., children, elders and people with respiratory system diseases). Increased lifetime exposure of tropospheric O₃ was a cause of decreased lung function in young adults (Targer et al., 2005). Air Quality Index (AQI) for air pollutants, in the US, is categorized into six Buadong et al. (2009) studied the association between O₃ exposure and hospital visits for cardiovascular diseases (CVD) in the central of BKK, Thailand. The study showed a positive relationship between exposure to O₃ on the previous day with increasing number of hospital visits for CVD in elderly patients (≥65 years). Fann et al (2011) studied the relationship between O₃ exposure with the national public health burden in the US and found O₃ associated with premature death in metropolitan areas where these numbers were greater than other habitable environs. The study of the Global Burden of Disease, Injuries, and Risk Factor study 2013 (GBD 2013) for 188 countries by Forouzanfar et al. (2015) reported the increased number of deaths during 1990 to 2013 (from 133 to 219 deaths in thousands) due to ambient O₃ pollution. World Health Organization (WHO) Regional Office for Europe, Economic Co-operation and Development (OECD) (2015) estimated the annual economic cost of premature deaths and those of morbidity from air pollution between US $1.431 trillion and $1.575 trillion across the countries of the WHO European Region.

For air pollutant species in the US, the AQI for each species is categorized into 6 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 US severity of O₃ concentrations in BMR are evaluated by AQI rating system for O₃. Table 3 provides the results of ambient air quality over BMR during 2010 to 2014 based on the following for Thailand: AQI of O₃. Based on the AQI for O₃ during the study period, the majority of air quality over BMR were in the good AQI category (~93.99%), followed by the moderate air quality category (~2.3%). However, unhealthy for sensitive group (~85.63%), unhealthy (~19.209%) and very unhealthy (2.59%)
hours (~0.04%) O₃ air quality categories were found during the study period. In general 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. Table (4) provides the ambient air quality over BMR during 2010 to 2014 based on the AQI of O₃. The calculation of the AQI for O₃ can be found in “AQI for O₃ 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 analysis (Aneja et al, 2001). The results from this study revealed evidence of violations for O₃ for air quality resulting in adverse health effects, human welfare, economics and environment over BMR. Source analysis suggests to control the first priority should be controlling pollution emissions from local sources that emit primarily from mobile sources should be the first priority. 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 contributes to 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 framework for the process of establishing an air quality policy while developing socioeconomic impacts.

4. Conclusion

Among measured gaseous criteria pollutants, O₃ is the only species whose concentrations frequently exceed the NAAQs of Thailand. The O₃ 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, which. On average, the number of hourly O₃ 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\textsubscript{3} exceedances at roadside sites demonstrates the effects of the titration of O\textsubscript{3} by NO played an important role due to decrease O\textsubscript{3} high concentrations. Interconversion between O\textsubscript{3} of NO and NO\textsubscript{2} and that were generally observed at this monitoring type (average [NO]\textsubscript{hourly} = ~166.0±19.8 ppb). Under photostationary state assumption, during dry season, the values of reaction rate coefficient of photochemical reaction shows that of NO\textsubscript{2} ($j_1$) and reaction rate coefficient of chemical reaction between NO and O\textsubscript{3} has a non-linear relationship with its precursor with high concentrations of O\textsubscript{3} which occur when ($k_1$) range from 0.12 to 1.22 min\textsuperscript{-1} and range from 28.3 to 30.9 ppm\textsuperscript{-1} min\textsuperscript{-1}, respectively. NO\textsubscript{x} concentration is less than values of about 60 ppb. After this point, marks the threshold for the interconversion between O\textsubscript{3}, NO and NO\textsubscript{2}. Under the low NO\textsubscript{x} regime ([NO\textsubscript{x}] < 60 ppb), O\textsubscript{3} concentrations is the dominant species; on the other hand, under the high NO\textsubscript{x} regime ([NO\textsubscript{x}] > 60 ppb), the concentrations of O\textsubscript{3} rapidly decrease, while NO\textsubscript{x} concentrations increase. Under high NO\textsubscript{x} regime, the concentration of O\textsubscript{3} is influenced by NO through the titration process. The result for the study shows that decreasing NO\textsubscript{x} emission will not directly decrease O\textsubscript{3} concentration over BMR. The regression curves reveal a background O\textsubscript{3} concentration of ~48 ppb (non-episode) and ~95 ppb (episode) over BMR. During O\textsubscript{3} episodes, the decrease of O\textsubscript{3} under the high NO\textsubscript{x} regime describes the important role of NO in destroying O\textsubscript{3} episode, both in the atmosphere in polluted environments. The local and regional contributions play an important role in the increase of O\textsubscript{x} concentrations. The result reveals that, decreasing emission from only local sources may not improve air quality during O\textsubscript{3} concentrations, under stagnant condition (wind speed < 4 m s\textsuperscript{-1}) and predominant wind directions (northerly, southerly and westerly winds) associate with elevated O\textsubscript{3} concentration in this area. During O\textsubscript{3} episodes, since the values of the local and regional air pollution transport contributes to O\textsubscript{2}-formation. Sources analysis suggests that to control pollution emission from local sources, the emissions from mobile roadside sources should be the first priority contributions were about double of those during non-episodes. Air Quality Index for O\textsubscript{3} reveals evidence of violations for O\textsubscript{3} for air quality resulting in adverse health effects, human welfare, economics and environment over BMR–air quality standards, in BMR, resulting in potential adverse health effects. To achieve O\textsubscript{3} reduction, control strategies may be needed. Emissions from mobile sources may be the first priority to manage O\textsubscript{3}, since BMR is more likely affected by mobile sources than point sources (CO/NO\textsubscript{x} = 19.8 and SO\textsubscript{2}/NO\textsubscript{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 O₃ 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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Tiwari, S., Dahiya, A., and Kumar, N.: Investigation into relationships among NO, NO₂, NOₓ, O₃, and CO at an urban background site in Delhi, India, Atmospheric Research, 157, 119-126, doi:10.1016/j.atmosres.2015.01.008, 2015.


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Figure 1: Map of BMR, including BKK monitoring station locations and five adjacent provinces, with the two major monsoons winds. The locations of three categories of (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 January 2014; ** the station has been closed since 1 August 2015; *** 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$_2$ and (d) O$_3$ and (e) NO from the 15 monitoring stations, during 2010 to 2014, are compared with the 1-hourly NAAQs (dotted line) of Thailand. Three different sites, the BKK sites, roadside sites and the BKK suburb sites are represented by light blue, purple and blue colors (except NO which is not a criteria pollutant). The number of hourly O$_3$ exceedances of hourly O$_3$ concentration are shown by (e) monitoring stations, (f) locations and (g) months and (h) seasons.
Figure 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.
Figure 4: Interconversion between O\textsubscript{3}, NO and NO\textsubscript{2}—Diurnal variations of rate of change of O\textsubscript{3} concentration (ΔO\textsubscript{3}/Δt) during a) local summer, b) wet season and c) local winter.
Fig. 10:00-16:00 LT for 2010 to 2014 (a) BKK sites, (b) relationship, crossover point and concentration distribution of NO, NO₂ and O₃ at a) BKK sites b) roadside sites and (c) BKK suburb sites. The polynomial regressions provide the crossover point for NOₓ (60 ppb).
Fig. 6: Effects of local and regional contributions on $O_3$ during non-episode and episode days over BMR. (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, 2010-2014.)
Figure 6
Fig. 8: Relationship between high O$_3$ concentration—the concentrations of O$_3$, wind speeds and wind directions during a) O$_3$ episodes ([O$_3$]$_{hourly} > 100$ ppb) (monitoring site ID is listed at the center of the Wind Rose Plots) and wind directions—and b) during non O$_3$ episodes ([O$_3$]$_{hourly} < 100$ ppb), over BMR during 2010 to 2014. The map illustrates several industrial areas located near the study area and the monitoring stations, blues, purples and dark blues identify BKK sites, roadside sites and BKK suburb sites; greys identify industrial areas.
Table 1: chemical rate coefficients ($k_j$) during winter and summer from the BKK sites, roadside and BKK suburb sites, 2010-2014

<table>
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<tr>
<th>Coefficient</th>
<th>Season</th>
<th>BKK sites</th>
<th>Roadside sites</th>
<th>BKK suburb sites</th>
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<tr>
<td>$k_3$ ppm⁻¹ min⁻¹</td>
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<td>Summer</td>
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<td>Summer</td>
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Table 2: the comparison of fitted linear regression from this study, including from BKK sites, roadside sites, and BKK suburb sites with other studies.
This study

- **BKK sites**  
  \[ \text{O}_x = 0.33\text{[NO}_x\text{]} + 44.39 \]  
  \[ \text{O}_x = 0.48\text{[NO}_x\text{]} + 91.10 \]

- **Roadside sites**  
  \[ \text{O}_x = 0.13\text{[NO}_x\text{]} + 53.89 \]  
  \[ \text{O}_x = 0.29\text{[NO}_x\text{]} + 104.45 \]

- **BKK suburb sites**  
  \[ \text{O}_x = 0.31\text{[NO}_x\text{]} + 47.0 \]  
  \[ \text{O}_x = 0.68\text{[NO}_x\text{]} + 82.89 \]

**UK**  
\[ \text{O}_x = 0.112097\text{[NO}_x\text{]} + 35.538.2 \]  
\[ \text{O}_x = 0.092112\text{[NO}_x\text{]} + 35.255.5 \]

**Buenos Aires, Argentina**  
\[ \text{O}_x = 0.099\text{[NO}_x\text{]} + 22.0 \]

**Delhi, India**  
\[ \text{O}_x = 0.54\text{[NO}_x\text{]} + 28.89 \]

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

**Table 32**: the comparison of CO/NO_x and SO_2/NO_x ratios from this study with other studies (modify from Rasheed et al., 2014)
### This study

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**Guwahati and Nagpur, India***

- > 0.3

**Kolkata, and Durgapur, India***

- < 0.13

Madrid City, Spain*

**Rouen City, France**

Islamabad, Pakistan

- Based on Emission Inventory, 2010

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- Based on Ambient Data

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* Fernandez-Jiménez et al., 2003

** Coppalle et al., 2001

*** Mallik and Lal, 2014

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**Table 43:** Number of hours that were found in different AQI categories of O₃ over the BMR during 2010 to 2014.
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