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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Assessment of Air Pollution in Bangkok Metropolitan Region, Thailand" *by* Pornpan Uttamang et al.

Anonymous Referee #1

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General comment

Pornpan Uttamang et al. have presented observations of CO, NO_x, SO_2 and O_3 from 15 monitoring sites at understudied Bangkok Metropolitan Region (BMR) for a five-year-long period from 2010-2014. Background pertaining to the air-quality in terms of PM and O_3 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.

Specific comments:

Title

Authors might consider making the title of the paper more specific. Authors assess CO, NO_x, SO_2 and O_3 air pollution and not overall air pollution in general.

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, NO_x, SO_2 and O_3. 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, O_3 exceedances, drivers for high ozone episodes and relationship of ozone production with NO_x/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!

Jinsart, W., Tamura, K., Loetkamonwit, S., Thepanondh, S., Karita, K., and Yano, E.: Roadside Particulate Air Pollution in Bangkok, Journal of the Air & Waste Management Association, 52, 1102-1110, *10.1080/10473289.2002.10470845*, 2002.

Suthawaree, J., Tajima, Y., Khunchornyakong, A., Kato, S., Sharp, A., and Kajii, Y.: Identification of volatile organic compounds in suburban Bangkok, Thailand and their potential for ozone formation, Atmospheric Research, 104-105, 245-254, *10.1016/j.atmosres.2011.10.019*, 2012.

Page 2, Line 23: Authors state "possible emission sources of pollutants that associate with O_3 formation are identified ". However, such identification is not discussed in the manuscript. Authors have only used the ratio of CO/NO_x and SO_2/NO_x 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.

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.

Page 3, line 22: What is the basis of the assumption that monitoring sites used were

representative of BMR specific patterns and trends?

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_x, SO_2 and O_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_x, SO_2 and O_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.

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?

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

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.

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].

Gaur, A., Tripathi, S. N., Kanawade, V. P., Tare, V., and Shukla, S. P.: Four-year measurements of trace gases (SO2, NOx, CO, and O3) at an urban location, Kanpur, in Northern India, Journal of Atmospheric Chemistry, 1-19, *10.1007/s10874-014-9295-8*, 2014.

Kumar, V., Sarkar, C., and Sinha, V.: Influence of post-harvest crop residue fires on surface ozone mixing ratios in the N.W. IGP analyzed using 2 years of continuous in situ trace gas measurements, J. Geophys. Res., 121, 3619–3633 *10.1002/2015JD024308*, 2016.

Naja, M., and Lal, S.: Surface ozone and precursor gases at Gadanki (13.5°N, 79.2°E),

a tropical rural site in India, Journal of Geophysical Research: Atmospheres, 107, *10.1029/2001jd000357*, 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.

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 trace gas mixing ratios near the surface in the Amazon Basin: Implications for the NO-NO_2-O_3 photostationary state and peroxy radical levels, Journal of Geophysical Research: Atmospheres, 117, *10.1029/2011JD016386*, 2012.

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.

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 tra-

jectories 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 $\sim$ 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 NO_x and low NO_x regime should be calculated based on the ratio of NO_x OH reactivity and VOC OH reactivity or using model calculated indicators (e.g. CH_2O/NO_y, H_2O_2/HNO_3 and $O_3/(NO_y–NO_x)$) as described by Kumar et al., [2011]. Classification based on cross over points are an oversimplification of the polynomial fits.

Kumar, R., Naja, M., Pfister, G. G., Barth, M. C., Wiedinmyer, C., and Brasseur, G. P.: Simulations over South Asia using the Weather Research and Forecasting model with Chemistry (WRF-Chem): chemistry evaluation and initial results, Geosci. Model Dev., 5, 619-648, *10.5194/gmd-5-619-2012*, 2012.

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_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_x and low SO_2/NO_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_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])

Garg, S., and Sinha, B.: Determining the contribution of long-range transport, regional and local source areas, to PM10 mass loading in Hessen, Germany using a novel multi-receptor based statistical approach, Atmospheric Environment, 167, 566-575, *10.1016/j.atmosenv.2017.08.029*, 2017.

The authors have referred to the work of Parrish et al. [1991] for local source identification using CO/NO_x ratio. However, longer-lived NO_y should be used in place of NO_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_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_2/NO_x ratios reported in Table 3. The SO_2/NO_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.

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 O_3 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 O_3 concentration could also be an alternative plot. How does

the wind rose look like for periods with O_3 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.

Section 3.6

Authors need to describe the calculation of air quality index. If they have used the simple hourly average O_3 concentration for calculation of AQI, then it is wrong. For calculation of hourly air quality index, O_3 concentration for a given 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.

Technical comments:

Page 1 Line 27 – page 2 line 2; Page 2, lines 11-16 These are better suited for site description.

Page 2, line 17: NO is Nitric oxide and not nitrogen oxide. Nitrogen oxides refer to the family of oxides of nitrogen.

Page 2, Line 20: What is the basis of the statement “Moreover, BMR experiences primarily O_3 exceedances amongst all the other gaseous criteria pollutants.”

Page 4, Line 4: Figure 1 should be mentioned earlier in the section.

Page 4, Line 20: What are the “equivalent instruments”?

Page 5, Line 3: Is the measurement period 2012-2014 or 2010-2014?

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

Page 6, line 5: Authors mention “ VOCs concentrations were measured periodically

only at one monitoring station limiting 5 its usefulness as part of this study ". However, Zhang et al. [2002] have reported CH_4 and NMVOC data from 10 out of 13 monitoring stations from BMR. Did the stations stopped monitoring CH_4 and NMVOCs?

Page 6, Line 12 and Figure 3: What is the explanation for a rather flat diel profile of NO_2 at roadside sites. Roadside sites are influenced maximum by traffic emissions, and one would expect a bimodal shape of diel profile.

Page 8, The rate constants and photolysis frequencies should be expressed in $cm^3 molecule^{-1} s^{-1}$ and s^{-1} respectively.

Page 9, line 9, The titration of O_3 with NO will not effectively reduce the O_3 concentrations. Such a titration process with produce NO_2 which will again photolyze in the daytime and produce O_3.

Page 12, line 2. Please check the lifetime of O_3. It should be few days (if not few weeks) in urban atmosphere.

Page 12, Line 15- Page 12, Line 5: Such description is better suited for introduction.

Page 13 Line 18 to page 19 line 2: Such discussion is well suited for outlook after proper restructuring.

Figure 1: I would recommend showing airmass back trajectories rather than showing wind directions with two indicator arrows.

Figure 2: Ambient variability should also be shown along with average values. Authors should also show the concentrations of NO, in addition to CO, SO_2, O_3, and NO_2. The colour for year 2010 and 2011 look same in panel "e".

Figure 3: Quality of figure should be improved (overall presentation, axis labels and legends). Ambient variability (as interquartile range or 1 σ standard deviation) should also be shown in addition to the average values. This should be done for other figures also in the paper.

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.

Table 1: Please refer to the comment for section 3.3.

Table 3: Authors should also include the SO_2/NO_x ratio reported from various cities in India for mobile sources as reported by Mallik and Lal, 2014.

Mallik, C., and Lal, S.: Seasonal characteristics of SO_2, NO_2, and CO emissions in and around the Indo-Gangetic Plain, Environmental Monitoring and Assessment, 186, 1295-1310, *10.1007/s10661-013-3458-y*, 2014.

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