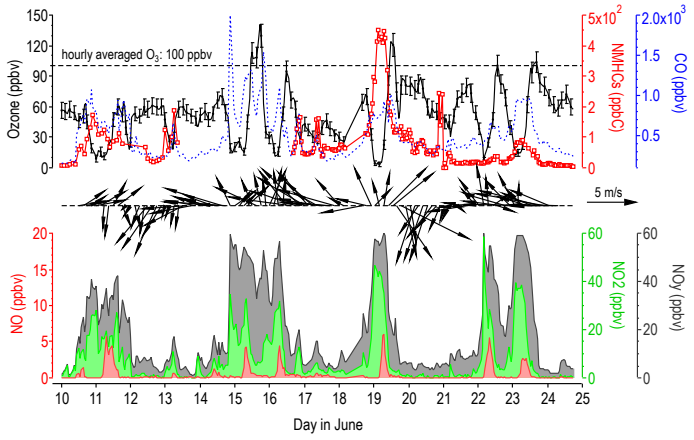
Reply to the comments of Anonymous Referee #1

We greatly appreciated the reviewer for providing insight comments and suggestions. We would like to modify our manuscript and clarify the discussions according to the specific comments. The detailed corrections are as follows:

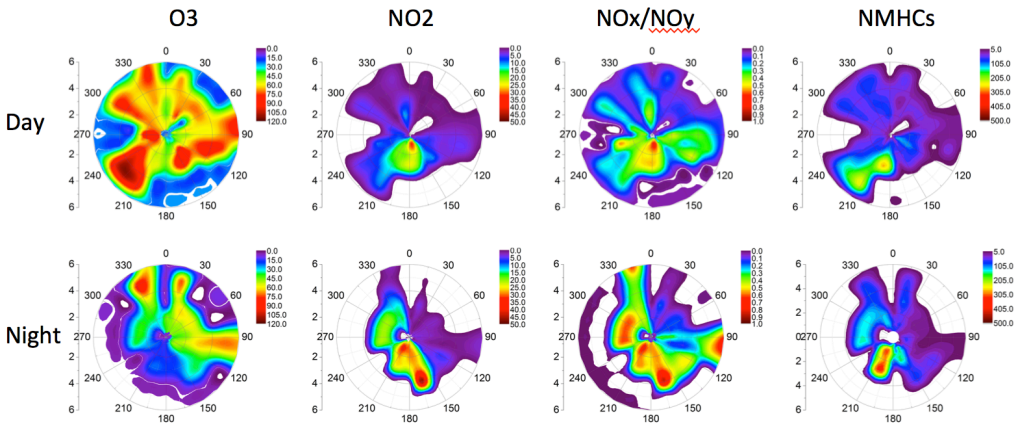
1. The paper argues that local anthropogenic emissions were very limited at the sampling site (page 30916, lines 26-27). It would be good to define what "local" means in this regard. The data in Figure 2 show that at high NOx, a very large fraction of NOy consists of NOx and ozone is titrated. This indicates that the sampled air masses at those times were only lightly aged, and had a significant contribution from local sources in addition to emissions from the Shanghai area 180 km South of the sampling site. The evidence thus appears to contradict the earlier statement that local anthropogenic emissions were very limited at the sampling site.

Reply: We will clarify this point in the revised manuscript according to referee's comments. Firstly, the NO_x emission at the observation site was very limited because the field campaign was performed in a "Science and Technology Park" (almost vacant and has no residence) near seashore area. I will revise the expression in page 30916, line 26-27. We agree with referee's comments that, the sampled air masses consisted of large fraction of NO_x and O_3 was titrated significantly, implying that the "local" source was greatly important. Within 40 km south of observation site, there are numbers of small county towns (e.g. Qidong, Latitude: 31.808°, Longitude: 121.658°), and the NO_x emission from these towns seemed also contribute to the high concentration of NO_x when southerly wind was prevailing (As shown in the revised Figure 2.). Additionally, to void misleading we will not point in particular to the impact of emission from Shanghai megacity on our observation because, except for Shanghai, there are numbers of big cities (population > 2 million) to the south of observation site (e.g. Natong, Latitude: 31.977°, Longitude: 120.900°, as shown in Figure 1), and the anthropogenic emission from industrial/residential area of these cities may also be responsible for the increase of NO_x and NMHCs at the site.



2. Figure 4 is interesting, but the information about the dependence of trace gas concentrations on wind direction and speed is convoluted with the dependence of all those parameters on the time of day. I suggest making similar graphs for the day- and night- time separately, when the site is most likely impacted by different sources.

Reply: As suggested, the dependences of O_3, NO_2, NO_x/NO_y and NMHCs on wind direction and speed for daytime (0800 – 1600 CST) and nighttime (1900 – 0500 CST) were plotted. As shown in the following figures, observation site was mostly impacted by the same source in the south in both daytime and nighttime. O_3 concentration in the daytime exceeded 100 ppb when air mass came from southwest. NO_2 and NMHCs also increase evidently; however at night, the O_3 concentration from southwest was extremely low, mostly due to titration reaction with NO_2 being emitted from urban area in the south. NO_x/NO_y ratio from south at night was generally larger than 0.5, indicating that the air mass was not very aged.



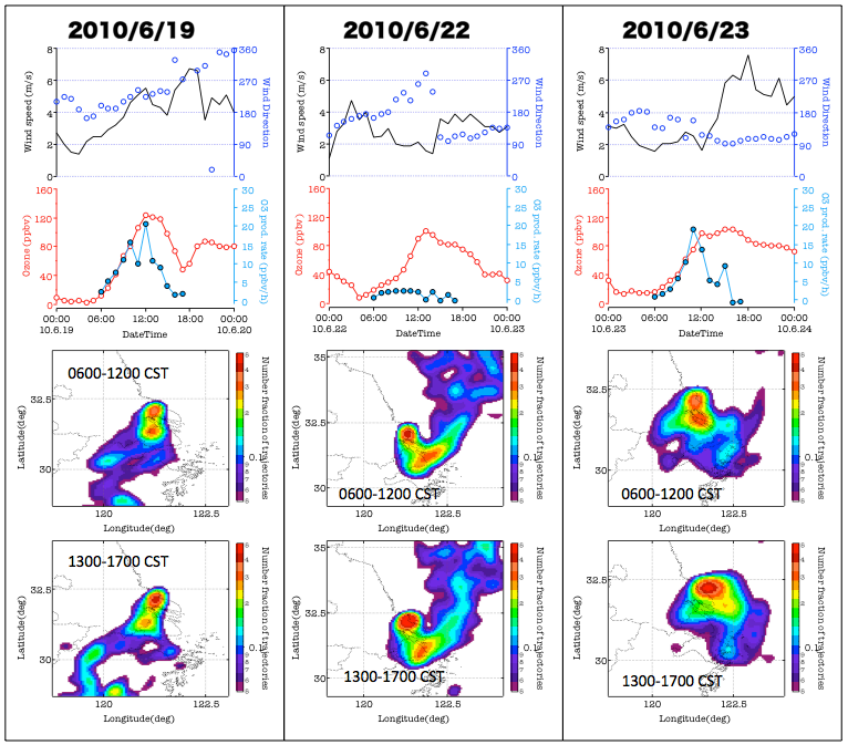
3. Section 5.1: it is interesting that the in-situ photochemical production rates of ozone are similar to the actual observed ozone increase rate during the day. However, this does not prove that a box model is adequate to explain the observations. I would weaken the conclusions of this section to reflect this. In addition, I would like to see more details on the diurnal variations in wind direction and speed to consider the relative importance of in-situ chemistry and transport. Given that the sampling site is on the coast, there may be land-sea breezes that could affect the ambient concentrations of trace species? In general, it is very dangerous to interpret observed increases in ozone at a ground site in terms of chemistry only, and the authors need to be much more cautious in this section.

Reply: We would like to follow reviewer's comments to revise the discussion in section 5.1. The diurnal variations of ambient O_3 concentration, O_3 net production rate on the basis of RACM2 model, and wind direction/speed were shown in the following figures. The relative importance of in-situ photochemistry and direct transport differed from case to case.

On June 19, the O_3 production rate reached its peak at 1200 CST when the site was prevailing moderate southwest wind (wind speed about 4 m/s). The accumulated O_3 production from 0600 CST to 1200 CST was only 73 ppbv, lower than the observed ambient O_3 concentration (124 ppbv, at 1200 CST). It indicated that less than 65 percent of the buildup of O_3 at observation site could be explained by in-situ photochemistry. In the afternoon, the O_3 concentration decreased quickly to 48 ppbv (at 1700 CST) when it changed to strong westerly wind (wind speed about 6 m/s), and total in-situ photochemical production of O_3 was 27 ppbv. It implied that the direct transport of O_3 was mainly responsible for the ambient O_3 level at the site. Footprint calculation (as shown in the figure 6f in the manuscript) indicated that the production of O_3 in the urban area in the south of observation site had great contribution.

On June 23, the O_3 production rate reached its peak at 1100 CST when the site was prevailing southerly wind. The 6-hour accumulated (0600 – 1100 CST) O_3 production at the site was 41 ppbv, only accounting for less than 50 percent of O_3 concentration (98 ppbv at 11 CST). Footprint analysis indicated of the great impact of O_3 formation/transport from the urban area in the south of observation site. In the afternoon, the wind direction shifted from south to east (the marine region) around 1200 CST and wind speed increase from 2 m/s to 6 m/s. Correspondingly, the O_3 production rate sharply decreased from 20 ppbv/hr to 5 ppbv/hr; however, the ambient O_3 concentration at the site still kept increasing and exceed 100 ppb (at1500 CST) on that day, and it was even as high as 77 ppbv at night (2300 CST). It indicated O_3 produced in the Yangtze River delta region in the daytime preserved over the marine area because of weak titration reaction between O_3 and NO_2, and they were directly transported to the observation site with easterly sea breeze at night.

On June 22, O_3 in the daytime at site was mostly attributed to direct transport because of only small fraction of O_3 was *in-situ* photochemically produced on the basis of RACM2 model. In the revised manuscript, O_3 production rate will be discussed in the combined analysis with wind information, and we will make clear that the both direct transport of O_3 and instantaneous photochemical production contributed to the high ambient O_3 level at the observation site.

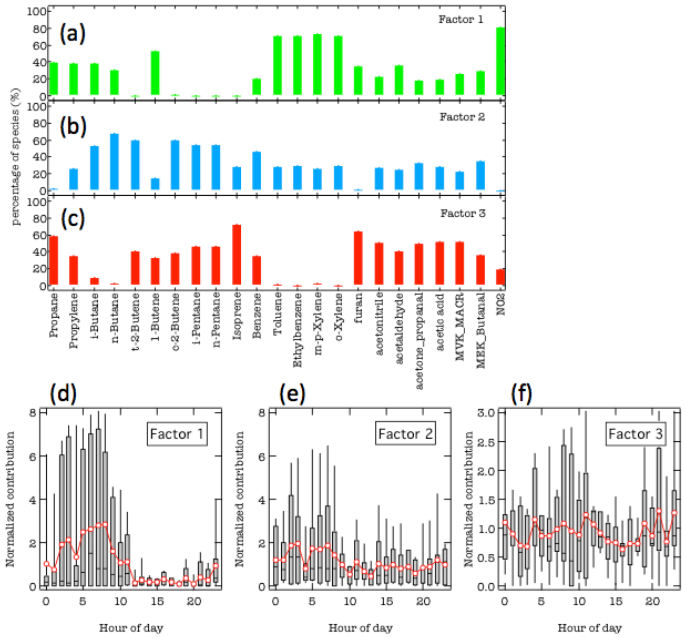


4. I found Figure 7 to be unclear. The isopleth in the background is clear, but what do the symbols, the symbol colors, the dashed and dotted lines, and the numbers along the x- and y-axes represent?

Reply: The circle and square symbols represent the calculated O_3 production rate on the basis of RACM2 model on June 19 and June 23, respectively. The dashed lines indicate the temporal variations of NO_x on these days. NMHCs/NO_x ratios, marked as the red-dotted lines and numbers in the lower-left corner of the plot, are used to reflect of the controlling region of O_3 production. We will clarify this in the figure caption of revised manuscript.

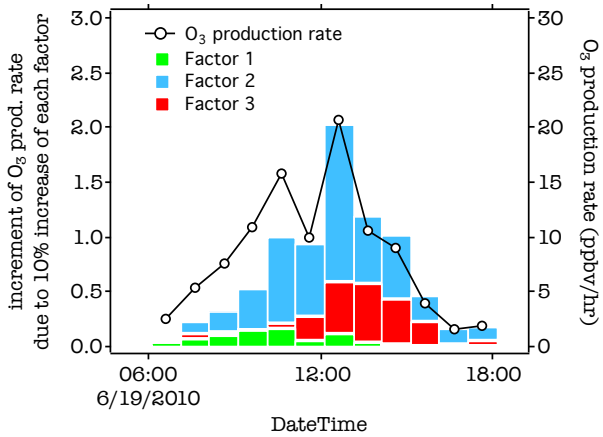
5. Section 5.4.1: I am worried that the other factors are influenced by chemical transformations in addition to different emission signatures. The authors have nicely shown that aged air masses from the Shanghai area are sampled at the site. In these air masses, the more reactive NMHCs will be more efficiently removed from the sampled air masses than the less reactive species. This chemistry leads to different time series for more and less reactive species and PMF can pick up on those differences and attribute more and less reactive species into different factors even though they come from the same source. Indeed, in the authors' analysis, the more reactive aromatics fall into factor 1, the less reactive alkanes in factors 3 and 4, and the least reactive benzene and propane in factor 6. The issue was investigated in a recent paper [Yuan et al., 2012], and I think the authors need to discuss the results from their PMF analysis in light of this issue.

Reply: We will revise section 5.4.1 in the manuscript according to reviewer's insight comment. As suggested by referee and literature [Yuan et al., 2012], the photochemical processes of more reactive VOC species during transport will affects the interpretation of PMF analysis, and the anthropogenic factor at different photochemical ages may mistakenly be attributed to independent sources. In the revised manuscript, we will reduce the PMF factor number from 6 to 3, and the previous explicit classification (such as vehicle, fuel evaporation etc.) is not used any more. The contribution of specified factor to the each specie (a-c), and diurnal variation (d-f) of each factor are shown in the following figure. The first factor contributed to large fraction of high-reactive species (e.g. C_8-C_9 aromatics, 1-butene) and NO_2, and we also found an obvious diurnal variation. Considering that NO_2 and C_8-C_9 aromatics have been much more abundant near the source, here factor 1 was termed as local primary factor. Factor 2 had abundance of low-weight alkanes and fewer fractions of high-reactive species and NO_2, and it did not show distinct diurnal variability. This factor correlated well with CO with a correlation coefficient of 0.63, we regarded the factor 2 as transport factor. The third factor was regarded as OBB-related sources due to the pronounced contribution of furan and acetonitrile to this factor with mass fractions of 64% and 50%, respectively. This factor also explained 72% of total isoprene, 51% of MVK + MACR (oxidation production of isoprene) and 52% of acetic acid. The discussion of their contribution to O_3 production in the section 5.4.2 will be on the basis of this classification.



6. Section 5.4.2: this analysis is not very convincing. In light of my previous comment, some of the source attribution may change. But also, what the analysis indicates to me is that the most reactive NMHCs simply do not reach the sampling site as efficiently in the afternoon. This does not imply that the more reactive NMHCs are less important for ozone formation in the afternoon. The same comment as before applies: it is dangerous to interpret the observed ozone in terms of in-situ formation only, whereas in reality the ozone at a site needs to be explained by a combination of the location and strength of the emissions, the transport of those emissions to the site and chemical transformations during the transport.

Reply: The discussion in this section will be modified in accordance to the new PMF classification. The increment of O_3 production rate due to 10% increase of each factor was calculated. In the revised manuscript, we will focus a typical heavy O_3 pollution case at June 19 (hourly-averaged ozone concentration: 124 ppbv and one minute value: 168 ppbv at 1400 CST) and discuss the relative importance of each factor on the in-situ photochemical formation of O_3. As shown in the following figure, the transport factor was responsible for 60% (43 ppb) of the in-situ photochemical production of O_3 in the morning, followed by that of local primary factor (23%, 17 ppb), and the OBB-related factor only counted for 17% of total O_3 production. In the afternoon, relative importance of OBB-related factor weighted and it explained 34% (12 ppb) of photochemical produced O_3. We will clarify the point in the manuscript that, transport factor took the major responsibility of the high ambient O_3 level at the observation site, because the reactive VOCs species might have been processed in the upstream area, which resulted in direct transport of O_3.



Minor comments:

1. Caption of Figure 3: I think the definitions of the blue and red symbols are reversed, i.e. red represents high ozone days and blue low ozone days?

Reply: red and blue symbols in the figure 3 represented high- O_3 and low- O_3 days, we will corrected it in the revised manuscript.

2. Page 30922, line 22: "broader" instead of "boarder".

Reply: The misspelling of word will be corrected.

3. Figure 6: do the footprints on the right refer to specific sampling times for the days shown? Or are they an average for the time periods shown? This was not clear to me. Also, much of the important information is actually in the different scales used for the y-axes, i.e. ozone production ranges from 0-40 ppbv/hr on June 19, but only from 0-6 ppbv/hr on June 12. It would be good to point that out clearly to the reader as it is easily overlooked.

Reply: To avoid misunderstanding of O_3 production rate on different days, the same scale of y-axes in the figure 6 will be used in the revised manuscript. And the residence time in the footprint plot will be changed to number fraction of backward trajectories in specific time period (0700- 1700 CST). The larger the fraction of number of trajectories in the grid the greater emission sources influence.