

## Reply to the comments of Anonymous Referee #2

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. P30917, L18, “Fifteen NMHCs species were detected . . . .”. At a site impacted by significant open biomass burning, the air should contain a lot of NMHCs and other VOCs with higher mixing ratios. Why only fifteen NMHCs were detected?

Reply: In the present study, NMHCs species were detected using an online gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC-MS). One of purpose of our field campaign was to clarify the contribution of OBB to O<sub>3</sub> pollution in YRDR. Therefore only main NMHC species relevant to O<sub>3</sub> chemistry was measured, and the detailed information about the measurements of NMHCs and OVOCs were published in the literature (Kudo, S., et al. (2014), Emissions of non-methane volatile organic compounds from open crop residue burning in the Yangtze River Delta region, China, *J. Geophys. Res. Atmos.*, 119, 7684–7698, doi:10.1002/2013JD021044.)

2. P30918, L16, “The missing data were linearly interpolated”. What was the portion of the missing data? Can the data interpolation impact your results?

Reply: The NMHCs species were measured at time resolution of 1~ 2 h, however the time step of input of RACM2 model was at time resolution of 5 minutes. For the convenience of model run, the data gap was linearly interpolated, and such treatment did not influence our results. During the observation period, the VOC data between June 13 and June 17 were missing because of instrumental maintenance. For the other high- O<sub>3</sub> pollution days, all the instruments were working well and the dataset was available for the RACM calculation. Actually, time interpolation of NMHCs data did impact our results.

3. P30919, equation (2), the summation sign in the last term is not necessary. However, it may be necessary to include reactions of NO<sub>2</sub> with some peroxy radicals, such as peroxyacetyl radical

Reply: The summation sign in the equation (2) will be removed. As suggested by referee, we did sensitive tests by including the peroxy-acetylnitrate formation reactions ( $\text{ACO}_3 + \text{NO}_2 \rightarrow \text{PAN}$ ,  $\text{RCO}_3 + \text{NO}_2 \rightarrow \text{PPN}$  and  $\text{ACP} + \text{NO}_2 \rightarrow \text{MPAN}$ ) and decomposition reaction ( $\text{PAN} \rightarrow \text{ACO}_3 + \text{NO}_2$ ,  $\text{PPN} \rightarrow \text{RCO}_3 + \text{NO}_2$  and  $\text{MPAN} \rightarrow \text{ACP} + \text{NO}_2$ ); however their influence on the simulation of O<sub>3</sub> production were ignorable. Here, we did not include these reactions in the present study.

4. P30922, section 4.2, how did you know the measurements were impacted by OBB? Was the burning near the site? If so, NO<sub>x</sub> from the OBB plumes may also be significant so that the OBB impact may be more important than the urban plumes transported from about 100 km away

Reply: we would like to clarify this point in the manuscript according to referee’s comments.

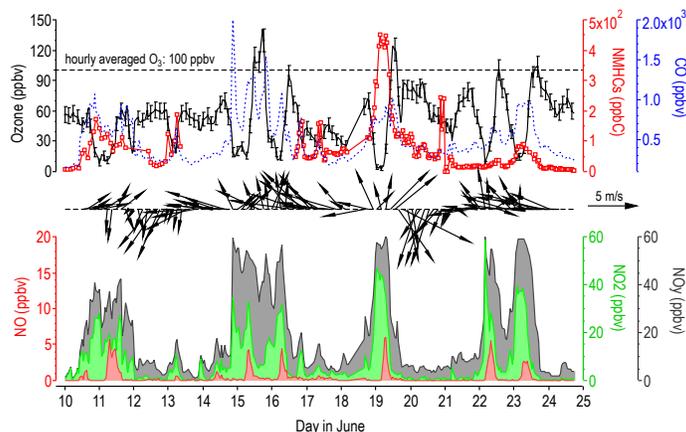
To the west of the observation site is the typical agriculture region, and open burning of agriculture residues sporadically occurred during our field campaign. Actually, the nearest open fires were about 1 km away from to the west of our observation site, and the flame and smoke was almost visible. The impact of OBB on the tropospheric carbonaceous aerosols and OVOCs loading have been reported in previous publications (1, 2).

1. Pan, X. L., et al., (2012), Emission ratio of carbonaceous aerosols observed near crop residual burning sources in a rural area of the Yangtze River Delta Region, China, *J. Geophys. Res.*, 117, D22304, doi:10.1029/2012JD018357.
2. Kudo, S., et al. (2014), Emissions of non- methane volatile organic compounds from open crop residue burning in the Yangtze River Delta region, China, *J. Geophys. Res.*, 119, 7684–7698, doi:10.1002/2013JD021044. )

To avoid misleading, we would like to make it clear that, except for Shanghai, there are numbers of big cities (population > 2 million) in the south of observation site (Natong, Wuxi, Suzhou, as shown in Figure 1 in the manuscript), and the pollutants emitted from industrial/residential area of these cities were also responsible for the increase of NO<sub>x</sub> and NMHCs at the site. In the revised manuscript, we will use “transported from urban areas to the south”, rather than specifying “Shanghai area” that is 100 km away.

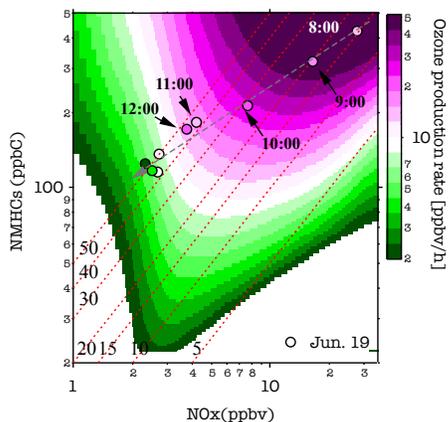
As mentioned by referee, biomass combustions emit NO<sub>x</sub>. However, it was hardly explain the long period (more than 12 hours), high troposphere NO<sub>x</sub> concentrations (~50 ppbv). Firstly, OBB normally emitted substantial amount of CO due to incomplete combustion processes. Sudden and sharp increase of CO concentration (dashed line in Figure 2) indicated the impact of OBB on our observation. However, we did not observe evident increase of NO<sub>x</sub> during OBB-impacting period.

Instead, the temporal variation of  $\text{NO}_x$  was more likely to reflect synoptic pollution processes. Secondly, we found that,  $\text{NO}_x$  concentration increased significantly when the air mass came from urban area to the south. Figure 2 illustrates the dependence of averaged  $\text{NO}_2$  concentrations as a function of wind speed and direction in the day and at night. It was clear that the  $\text{NO}_2$  emission from south was mostly responsible for the  $\text{NO}_2$  at site, and the emission of  $\text{NO}_x$  from OBB was less important than that from anthropogenic emission in the urban area.



5. The paragraph between P30925 (L 26) and P30926 (L9), and Figures 6 and 7. I disagree with your statements. Based on Figures 6 and 7, I think O<sub>3</sub> production on 19 June 2010 changed from VOCs-controlling to VOCs- and NO<sub>x</sub>-controlling, and that on 23 June 2010 was VOCs-controlling.

Reply: I will make it clear the discussion about the O<sub>3</sub> production sensitivity, and we marked the time of day for the case on 19 June 2010. As shown in Figure 7, the O<sub>3</sub> production in the morning was sensitive to both NO<sub>x</sub> and VOCs; however decrease of NO<sub>x</sub> concentration by 50% resulted in increase of O<sub>3</sub> (as shown in blue dash line), and decrease of VOCs concentration by 50% resulted in evident decrease of O<sub>3</sub> production (blue line). It indicated that reduction VOCs in the morning was more effective to reduce the risk of high O<sub>3</sub> pollution; therefore we defined this period as “VOCs-controlling” and it was “NO<sub>x</sub>-controlling” in the afternoon. For the case on 23 June 2010, we could see similar variability of O<sub>3</sub> productions by changing the NO<sub>x</sub> or VOCs concentration, and O<sub>3</sub> production regime shifted from VOCs- controlling to NO<sub>x</sub>- controlling on 1200 CST. In the revised manuscript, we will remove the case on 23 June 2010 from the figure 7 because, the O<sub>3</sub> production isopleth diagram was derived on the basis of a series of model runs that was constrained by the mixing ratio of O<sub>3</sub>, NO<sub>x</sub>, and VOCs, J values, and meteorological data observed at 10:00LST on 19 June. The O<sub>3</sub> production isopleth diagram on 23 June 2010 may be slightly different.



6. Section 5.4.1, are these results from Kudo et al. (2014)? The number of samples for the PMF analysis should be given. Very reactive species, such as isoprene, NO<sub>2</sub>, etc., were used in the PMF calculations. Such species may be largely reduced (NO<sub>2</sub> may also be produced) during the transport from the sources to the observation site. How did you treat this influence? What is the impact of this problem on the results? You attribute Factor 5 to vehicular-exhaust, but we know that VOCs are co-emitted by vehicles. Are there coal-fired power plants in the surrounding area? If there are, they may be major contributor to NO<sub>x</sub>.

Reply: We will modify the discussion in the section 5.4.1 and section 5.4.2 in the revised manuscript. In the present study, 206 samples were used in PMF analysis. As suggested by referee, the photochemical processes of more reactive VOC species and NO<sub>2</sub> during transport will affect 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 first factor contributed to large fraction of high-reactive species (e.g. C<sub>8</sub>-C<sub>9</sub> aromatics, 1-butene) and NO<sub>2</sub>, and we also found an obvious diurnal variation. Considering that NO<sub>2</sub> and C<sub>8</sub>-C<sub>9</sub> 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<sub>2</sub>, 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<sub>3</sub> production in the section 5.4.2 will be on the basis of this classification.

7. P30916, L8, delete “anthropogenic”.

Reply: We delete “anthropogenic” in the revised manuscript

8. P30916, L15-16, “from the middle of May to the end of June”. Which year? In other places you use “June 2010”.

Reply: We will use “from the middle of May to the end of June, 2010” and I will keep consistency throughout the context.

9. P30916, L26-27, exchange the sentence “Local anthropogenic emissions in the Science and Technology park were very limited” with that after it.

Reply: We will clarify this sentence in the revised manuscript.

10. P30917, L16, delete “mass”.

Reply: The word “mass” will be deleted in the revised manuscript.

11. P30917, L28, “Ionico” should be “Tonicon”.

Reply: The word “Ionico” will be replaced with “Tonicon”

12. P30923, L8, delete “(not including oxygenated VOCs)”. It is by definition clear that NHMC does not include oxygenated VOCs.

Reply: The sentence “not including oxygenated VOCs” will be deleted.

13. P30924, L19, “at 11:00 LST”? I think it is “at 12:00LST”.

Reply: it will be changed to “at 12:00 LST”

14. P30925, L3-4, how did obtain “the observed O<sub>3</sub> production (151 ppbv)”?

Reply: We will change the discussion in this part. On June 22, mixing ratio of O<sub>3</sub> on a daily basis was 151 ppbv (sum of total mixing ratio of O<sub>3</sub> from 06:00 to 17:00, subtracting a background value ~25 ppbv), however only small fraction of O<sub>3</sub> (17 ppbv on a daily basis) was *in-situ* photochemically produced on the basis of RACM2 model. It suggested that O<sub>3</sub> in the daytime at observation site was owing to direct transport from upstream area.

15. Table 1, units are missing. And you cannot say “the mixing ratio of black carbon (BC)”.

Reply: I will add a unit of black carbon concentration in Table 1.