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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Examining the major contributors and controlling factors of ozone production in a rural area of the Yangtze River Delta region during harvest season" *by* X. Pan et al.

Anonymous Referee #1

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This is an interesting paper that analyzes measurements of ozone, NOx and NMHCs at a coastal site in China to the north of the Shanghai metropolitan area. The authors describe the general features of the data set and use a box model to investigate the efficiency of in-situ ozone formation. They also use positive matrix factorization for source attribution of the emission sources. The paper is well written and the graphs are mostly clear and well done. I have several major and a few minor comments that I believe the authors need to address before the paper can be accepted.

Major comments:

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.

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 nighttime separately, when the site is most likely impacted by different sources.

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.

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?

5. Section 5.4.1: some of the results from the PMF are interesting and make sense,

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for example that furan and acetonitrile are attributed to one factor that may be related to biomass burning. However, 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.

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.

Minor comments:

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?

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

Figure 6: do the footprints on the right refer to specific sampling times for the days

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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.

References

Yuan, B. et al. (2012), Volatile organic compounds (VOCs) in urban air: how chemistry affects the interpretation of positive matrix factorization (PMF) analysis, J. Geophys. Res.-Atmos., 117, D24302, doi:10.1029/2012JD018236.

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