Zhao et al. describe VOC measurements conducted at the Jiangsu Academy of Environmental Science (JAES) in Nanjin, China. The authors measure VOCs using a GC system, and interpret the sources of these VOCs using positive matrix factorization. The authors evaluate the environmental impacts of these emissions on ozone formation using an observation-based model (OBM) employing the Master Chemical Mechanism (MCM v3.2), and identify the anthropogenic VOCs likely to be significant ozone precursors. The authors also evaluate ozone sensitivities to VOC and NOx reductions, and conclude that VOC reductions would be the best strategy to reduce ozone in Nanjing.

In general, the manuscript reads very well and is well-organized to tell a coherent message. I appreciate the authors work to carefully measure VOCs and benchmark these measurements against other cities in China. I am generally convinced by the PMF results given that the authors interpretation is reasonable, and the PMF factors are prescribed to obvious sources in the Nanjing area (which are very well described); however, I do have some recommendations that could improve the PMF analysis and strengthen the justification of source apportionment. Finally, I believe the use of the OBM is justified to evaluate VOC RIR, but I am not convinced that the OBM can be used to evaluate the ozone isopleth without further evidence that the model is doing an adequate job to capture ozone formation in the Najning region. My comments below primarily address PMF and the OMB.

<u>Major comments</u>

1. The PMF solution appears to be reasonable; however, I believe the authors need to do more to show that the PMF solution is robust. In Section 2.2, the authors state that comparisons were made to observations, emissions inventories, and previous PMF analyses, but no evidence is shown here or in the supplement to convince the reader that this is true. Can the authors show the Q/Qexp and explain why they settled on a 5-factor solution? What was the factor space used? Did the authors vary other parameters (e.g. Fpeak) or conduct a bootstrapping analysis to estimate uncertainty? Can the authors show the comparisons to other factor profiles reported in literature (e.g. the industrial factor compared to An et al. 2014)?

   I ask because PMF is partly subjective, and a more thorough discussion is necessary to justify why the authors settle on the solution presented in the manuscript. A 5-factor solution seems reasonable, and the factors discussed all appear to be consistent with the sources surrounding the sampling site, but this should be shown with more evidence in the main text or supplemental information.

2. The authors employ an OBM to evaluate ozone sensitivity to VOCs and NOx. OBMs are primarily useful because they allow one to evaluate relative incremental reactivity (as the authors describe in Section 2.3). One strength of an OBM is that you do not need all of the measurements that describe ozone formation; rather, you calculate source functions that explain residual effects on the time evolution of a measured species (e.g. meteorology, chemistry not accounted for in the mechanism, additional precursors that contribute to

ozone formation, etc). From these calculations, you can derive the RIR by conducting a small perturbation on the system (e.g., decreasing or increasing the concentration of a species that is measured and well-represented by the model). The calculations of RIR are good and justified with the use of an OBM.

In Section 3.4, the authors extend this analysis to evaluate the ozone isopleth. In this context, I don't believe the use of an OBM is justified. Isopleth calculations are defendable if a large fraction of the local, photochemically produced ozone is explained by the measured precursors. If a significant fraction of this produced ozone is explained by the time-dependent source function (i.e., the "residual" ozone), then the authors may not be measuring (or including in the model) a significant fraction of the VOC precursors needed to derive ozone formation. In that case, how can the authors determine whether Nanjing is VOC or NOx-sensitive? The isopleth presented in Fig. 6 is very NOx saturated, which the authors say generally agrees with previous literature. But do the measurements really defend this? The argument that Nan

If the authors are to present an ozone isopleth, then I believe there needs to be a much larger discussion describing how well the OBM performs in reproducing observed ozone mixing ratios. Without much discussion, I can only assume that there is residual ozone that is explained by the time-dependent source functions derived through OBM calculations, and not by the precursors measured by GC. How much of the ozone calculated via OBM is explained by the precursors measured by the GC, and how much of the ozone is unexplained? Can the authors show an analysis (perhaps just a time series) showing ozone explained by the precursors, and ozone explained by the source function? This helps place into context the extent to which the measured VOCs were the primary contributors to ozone observed at the ground site.

Finally, the authors also need to provide more details about the OBM itself. The only description of how the model was tailored to the Nanjing observations is provided at lines 135-140. What meteorological conditions were used? If this is observation-based, I assume that dilution by PBL expansion and wind speed are lumped into the source functions, but what about incident solar radiation? How do the authors calculate photolysis frequencies? Did the authors use a model, such as TUV, or was there a solar spectrum measurement? Can the authors provide a jNO2 frequency to orient the reader? The authors constrain CO, NOx, SO2, and O3. How were these species measured, what instrumentation, and how was this instrumentation calibrated? Finally, when were the O3 episodes? A time series showing ozone over the course of the campaign would be helpful.

Other comments

Line 112: PMF can be conducted using many tools. Is this the US EPA model, SoFi, another model, or one that was developed by Yuan et al. or Ling et al.? This should be noted here, with a relevant reference if necessary.

Line 120: Shao et al. discuss VOC reactivity through analysis of maximum incremental reactivity (MIR) and by calculating propylene-equivalent concentration. Which method are you referring to?

Line 130: please provide references for the MCM (see the following website for appropriate references depending on the sub mechanisms used: http://mcm.leeds.ac.uk/MCMv3.2/citation.htt).

Also, is there a reason that v 3.2 was used, rather than 3.3.1? v3.3.1 has updates to the isoprene mechanism that may (or may not) be relevant here.

Line 164: By TVOC, you mean the sum of measured VOCs?

Line 172: Is this reversed? The first number (referring to weekdays) is lower than the second (referring to weekends).

Table 1: You only give an average and standard deviation - no mixing ratio ranges are shown. I recommend removing "range"

Line 194: Continuous VOC measurements have been available much longer than this in other countries. I would recommend changing this wording to say "online VOC measurements have been available for multiple decades"

Fig 2. This is a nice benchmark of the Nanjing measurements with other cities during a period when developed countries were still reducing mobile emissions (mid 1990s - early 2000s). How does this compare with measurements conducted in developed countries today? It would be nice to see how the mixture in Nanjing compares to London or Los Angeles today, and would also highlight the gap that could be achieved with further VOC reductions.

Lines 227-228: Can the authors briefly summarize the conclusions from Wang et al. 2013? Was it due to changes in prevailing winds, or simply due to a buildup of pollutants during strong inversions?

Line 280-281: As the authors note, these differences result, in part, due to the proximity of the different sampling campaigns. However, I think it's also good to note why these differences are important. How much of the population resides in the sampled region? Is the mix measured in a more residential area more important for human exposure? This is certainly a nice motivation to look at the spatial VOC distributions in Nanjing in the future.

Line 319: Do you mean that you averaged the PMF solutions during the ozone episodes and non-episode days to look at differences?

Figure 6. The isopleth description is somewhat confusing - is this % change in NOx and VOCs, or % of base-case VOCs?

Section 3.5. Without more work to convince the reader that the ozone isopleth is reasonable, I believe these statements would need to be amended. First, the authors haven't shown that the ozone precursors measured account for the majority of the ozone modeled in the OBM. Second, the recommendation to prioritize VOC reductions (line 381) is very likely to matter on a local level (as alluded to by the authors), but what about ozone formation on regional scales? In other countries, downwind of major cities, ozone formation transitions to NOx-sensitive due to the abundance of biogenic sources that can react alongside NOx (e.g. Trainer et al., 1987). I think this should be discussed as well, since NOx reductions matter and are important in the long run.

Minor Comments

Line 19: It would be good to note that the measurements at JAES were conducted using GC.

Lines 23-24: Awkward phrasing, recommend saying "We identified VOC sources using positive matrix factorization and assessed their contributions to photochemical O3 formation using an observation-based model employing the MCM"

Line 30: "control on" seems strong, given that other factors (e.g. meteorology) play a very important role. May suggest using "precursor to"

Line 32-33: Do you mean that the contribution of biogenic emissions to O3 was significantly lower than anthropogenic emissions? It would be useful to make this comparison.

Lines 45-48: The word "associated" suggests that rapid economic growth occurred because of increases in pollution. Would recommend replacing associated with "Rapid economic growth has led to ..."

Line 56: "VOCs" should be singular, since it is used as an adjective here. Other instances of this are found sparsely throughout the text.

Line 62: What do you mean by "industrial structure"? Does you mean that there is a high presence of industry in Ningbo?

Line 76: You could clarify here that you employ the entire MCM (v 3.2).

Line 78-79: Summarized, proposed, and assessed should be present tense here, since you are recommending these in the present manuscript

Line 100: When you say "the sample was enriched after 600 mL of air sample" do you mean "600 mL of air was sampled"? If so, the latter phrasing may be more clear.

Line 101: What is the "Dean's Switch" technology?

Line 107: Was this a custom calibration standard, or a commercially available standard? If commercially available, it would be good to quote the manufacturer. If prepared in-house, are there uncertainties in the VOC mixture?

Line 245: “Identified” is a Confusing word choice, since you identified the sources, not the model! I would recommend changing to "Five VOC sources were resolved by PMF"

References

Trainer, M., Williams, E., Parrish, D. *et al.* Models and observations of the impact of natural hydrocarbons on rural ozone. *Nature* **329,** 705–707 (1987) doi:10.1038/329705a0