Letter of Responses

Manuscript: Impact of pollution controls in Beijing on atmospheric oxygenated volatile organic compounds (OVOCs) during the 2008 Olympic Games: observation and modeling implications (Ref. No.: acp-2014-620)

Reply to Referee #1

We thank Referee #1 for his/her comments on our manuscript, which help us to re-think some details and improve the quality of the paper. Below, we reply the reviewer's comments point by point.

Summary

As the title suggests, this paper examines the response of oVOC to large-scale emission reductions implemented in Beijing during the summer Olympics. This event was a prime experimental opportunity, and despite a number of other papers having been published on this topic, the current manuscript offers some new and unique elements. In particular, the use of a neural network to separate the effects of meteorology and emissions reductions on oVOC changes is a novel approach that sidesteps the need to explicitly model various processes.
The subject matter is appropriate for ACP. The English is fair but could be improved in places. I recommend this paper for publication in ACP after consideration of the following minor revisions.

Response: Thanks, the encouragement is appreciated.

General Comments

Section 3.3: It was not clear to me, at the outset, how the discussion of emission ratios tied in to the previous discussion of control measures. On a second glance I see the phrase "source patterns," but this is somewhat ambiguous. It should be made clearer in the first paragraph that the goal of this analysis is to determine whether the controls, in addition to changing the total emission amounts, also altered the relative emission of OVOC precursors.

Response: We accepted the reviewer's suggestion and re-arranged the section 3.3 in the revised manuscript. The description of the goal of emission ratios has been added to the first paragraph of section 3.3, as follows: "As NMHCs play significant roles on the formation of secondary OVOCs, emission ratios of NMHCs before and during the full control were compared in this section to determine whether the emission

restrictions also altered the relative emission of OVOC precursors (i.e. source pattern of NMCHs), in addition to reducing their total emission amounts."

Specific Comments

P26132, L4: impacts have also been evaluated from satellite observations. I suggest adding a few references for this aspect as well.

Response: Thanks for your suggestion and accepted. Several previous papers on satellite observations for NOx, CO and aerosol during the Olympic Games (Witte et al., 2009;Worden et al., 2012;Lyapustin et al., 2011) have been cited in the revised manuscript.

P26137, L10: It is stated that the neural network adequately reproduces the validation data, but I think this needs to be shown – perhaps as some scatter plots in the supplement. At the very least, it needs to be quantified, e.g. as a % accuracy.

Response: Accepted. The correlation coefficient (R) between the observed and predicted values of ln([VOC]) for each compound in the validation dataset was tabulated in Table S1, and scatter plots for two NMHCs and four OVOCs are now provided in the supplement as shown Fig. S3.

P26145, L26: The Li et al. (2013) paper speculated that aerosol sinks *might* be important for HCHO, but they did not prove it. This sentence should be modified to reflect the distinction.

Response: Accepted. The sentence has been re-written. In the revised manuscript, the loss of aldehydes on aerosols through heterogeneous uptake processes was included in M3 and M4 by using the uptake coefficient of 10^{-3} for two aldehydes. On average, the modelled HCHO and CH3CHO by M3 were decreased by 64% and 58%, respectively, compared to M2. Therefore, the loss of aldehydes on aerosol particles might be important in the polluted areas with high production rates of aerosols. Further research on sinks of aldehydes, particularly for heterogeneous uptake processes, is still needed in future studies.

P 26145: On the same topic, the overprediction of HCHO, even with "corrected" deposition and dilution, is staggering. The authors suggest that sinks are to blame, but what about sources? If OH is overpredicted by 30% as suggested by Fig. 6a, this should have a marked effect on oVOC. An additional model simulation using "calculated" OH profile would provide a sensitivity test for this.

Response: Thanks for pointing out the unreasonable statement and suggestion. As the uptake of aldehydes by aerosol surface was considered in the revised manuscript, we re-compared the modelled and calculated OH and found that the over-prediction of OH in the daytime is aound 22%. As the uncertainty of OH measurement and $J(O^1D)$ measurement is 20% and 10%, respectively, from Lu et al. (2013), in addition to a fitting error between OH and $J(O^1D)$, the difference between the modelled and calculated OH is acceptable. Also it is hard to say that the calculated OH from empirical function would be more accurate than the modelled results.

As the reviewer suggested, we ran the model using calculated OH, and found the averaged concentrations of HCHO, CH3CHO, MVK+MACR, acetone, MEK were changed by 2.98%, 3.07%, -8.39%, 0.25% and 1.04%, respectively, compared with M4. Therefore, the difference between two models with modelled and calculated OH could be neglected.

P26146, L4-10: What kind of sinks would be consistent with MVK+MACR only being over-predicted in the afternoon? Also, I would not say that the model predicts "nocturnal productions," but rather that it does an OK job of representing nocturnal sinks (which presumably are mostly deposition?).

Response: The decreased MVK+MACR in the afternoon might be due to the unexpected high deposition by vegetation at that time. As reported in Karl et al. (2010), in tropical ecosystems the observed deposition velocities for MVK+MACR were up to 2.4 cm/s, 3-4 times higher than what was used in our model runs (0.6-0.8 cm/s). And they found that the uptake of MVK+MACR by vegetation followed an exponential increase with leaf temperature, and a light dependency as well. So, more MVK+MACR would deposit on leaves in the afternoon, which gives evidence of the gap between modelled and observsed MVK+MACR during that period. In the revised manuscript, the discussion in Section 4.2.2 was modified accordingly.

Thanks for pointing out the inappropriate expression about "nocturnal productions" for MVK+MACR. We accepted and corrected it in the revised version.

P26146, L26: Is the primary source of acetone associated with combustion? If not, it is probably not appropriate to use CO as the normalization factor for incorporating emissions. It might be more appropriate to use a constrained NMHC that comes from the same source.

Response: Agreed. Combustion source is one of the primary sources of acetone in urban areas, but acetone also directly comes from solvent usage and evaporation, particularly in chemical processing procedures. In this study, we attempted to estimate

the contribution of primary sources to ambient OVOCs based on emission ratios of OVOCs versus CO and measured CO, assuming that the consumption of CO can be ignored compared with OVOCs (owing to CO's long atmospheric lifetime). Thus, it is necessary to find a slightly reactive or inert species to work as an indicator of primary emissions. CO and acetylene are frequently used as reference compounds in emission ratios (de Gouw et al., 2005;Warneke et al., 2007;Borbon et al., 2013;Yuan et al., 2012;Wang et al., 2014), as they are relatively inert compounds and come most from automobile exhaust and fuel combustion, the dominant sources of VOCs in cities. But these two species are seldom observed in solvent usage. Other relatively inert VOCs such as ethane and propane show more variable emission ratios for different sources, so they are also not suitable to be the unique tracer of non-combustion sources. Thus, we have to say, at current stage it's hard to find an appropriate tracer for evaporation sources to work as the reference in emission ratios. In future study, we plan to conduct direct measurements on OVOCs sources, and try to find out more appropriate compounds to meet our requests.

The discussion related to primary acetone in Section 4.2.3 has been modified in the revised manuscript.

P26149, L10: why are the modeled changes in acetone so big? Is it due to one particular class of VOC, and does this imply that the model is misrepresenting secondary acetone production?

Response: The big difference between modelled acetone concentrations of M1 and M2 (or M3) is probably due to the addition of vertical dilution and different deposition rate. The dry deposition rate of acetone used in M1 is 1.2 cm/s, and 0.55 cm/s for M2 and M3. Therefore, the model scenario M1 with faster deposition presented lower concentrations during the nighttime. By taking consideration of vertical dilution, the modelled concentration of M2 (or M3) was decreasing for the period of 6:00-10:00, then coming up again, so the afternoon peak in M2 and M3 was about one hour delayed from M1.

Technical Comments

P26130, L22: suggest splitting this into two sentences.

Response: Accepted and corrected.

P26131, L10: and how OVOCs

Response: Accepted and corrected. The sentence is corrected to "create a valuable

opportunity for studying how OVOCs respond to the emission reductions…".

P26131, L21: "Great efforts of transport sector" is an awkward phrase.

Response: Accepted. The sentence has been changed to "Nearly 2 million vehicles were banned from the roads step by step…" in the revised manuscript.

P26132, L5: dramatic

Response: Accepted and corrected.

P26133, L2: delete "random"

Response: Accepted and corrected.

P26133, L16: northwest

Response: Accepted and corrected.

P26135, L13: do you mean alkylcyclohexanes?

Response: It should be cycloalkanes, thanks for pointing out the error.

P26137, L2: previous day v

Response: Accepted and corrected.

P26138, L4: I would recommend changing this sentence to read "Several additional model scenarios were constructed to test the sensitivity of simulated OVOC concentrations to assumed deposition rates and boundary layer evolution."

Response: Thanks for your suggestion, we accepted and changed the sentence accordingly in the revised version.

P26139, L19: aromatics

Response: Accepted. The additional "aromatics" is deleted in the revised manuscript.

P26143, L3: reflect the similarity

Response: Accepted and corrected.

P26143, L20: “is of similarities” is awkward.

Response: Accepted, and the sentence was modified to “…indicating that emission patterns of automobile source in different cities showed a similarity.” in the revised manuscript.

P26145, L24: are consistent with

Response: Accepted and corrected.

P 26147: Table 5 is presented before Table 4 in the text, so their order should be switched.

Response: Accepted and corrected.

Tables 2 and S1: Caption should include a definition for P(t).

Response: Accepted. The explanation for P(t) has been added to the caption, as “where P(t)<0.05 implies that the difference in the two datasets is statistically significant at the confidence level of 95%.”

Figure 4: since you subtracted background CO, the y axis labels should read ΔCO

Response: Accepted. The y-axis labels in Fig.4. have been corrected accordingly.

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