

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 NO_x, 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, especially 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 around 22%. As the uncertainty of OH measurement and $J(\text{O}^1\text{D})$ measurement is 20% and 10%, respectively, from Lu et al. (2013), in addition to a fitting error between OH and $J(\text{O}^1\text{D})$, 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 observed 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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Reply to Referee #2

We thank Referee #2 for his/her comments on our manuscript, which suggested us to reconsider some details of box model and helped us to improve the quality of the paper. Below, we answer the reviewer's questions point by point.

OVOC observations during the Olympics Games in 2008 and summer 2005 were analyzed using statistics methods and box-model simulations. The analysis treatment is comprehensive. The emission reductions during the Olympics Games allowed the authors to analyze the mechanisms that control OVOCs in Beijing and hence mega cities in China in general. While I support the eventual publication of this paper, there are several places where the paper can be improved.

- (1) Through the analysis of sections 4.2, 4.3, and 4.4, some general conclusions can be given on the relative importance of photochemical production, primary emission, dry deposition (and other losses), and transport to major OVOCs (such as HCHO, acetaldehyde, and acetone). Statements like "This discrepancy is mainly attributed to missing sinks, such as vertical dilution, transport, and heterogeneous uptake on aerosols." (P. 26147) and "However, the model was not able to predict acetone because of transport effect or local emissions." (in the conclusion section) are too general.

Response: It is true that the current box model could not well reproduce the measured OVOCs concentrations, it predicts higher aldehydes. The results from different scenarios showed that primary emission of OVOCs, uptake of aldehydes by aerosols, and other physical processes (e.g. dry deposition, boundary layer height, vertical dilution) contributed to the discrepancy. In the revised manuscript, the uptake of aldehydes by particle surface and primary sources for anthropogenic OVOCs were quantitatively estimated in Section 4.2. And those general conclusions are avoided and modified by some specific results with numbers.

- (2) The comparison of Table 2 and Figures 2 and 3 should focus on daytime only for OVOCs since the focus of this paper is on secondary production of OVOCs, which occurs mainly in daytime. Separating day and night in Table 5 is nicely done.

Response: The first goal of this study is to estimate the impact of reduced emissions on ambient OVOCs during the summer of 2008, so the changes during the nighttime should be included. Table 2 and Fig.1-2 gives a whole picture of the study. Secondly, this study attempts to reproduce the changes of OVOCs using the box model by

increasing the concentrations of precursor NMHCs and other gasses, and to compare the secondary formation of OVOCs for the two periods. Because of the difference of daytime and nighttime chemistry of VOCs, the production rates of HCHO are discussed by separating day and night in Table5 (now Table 4 in the revised manuscript).

- (3) The dry deposition velocities used in M2 are more reasonable than M0 and M1. Why not use those in M0 and M1 too?

Response: The dry deposition velocities in M0 are a basic setup for a box model which is also used in some previous studies (Li et al., 2014; Lu et al., 2013). We didn't merge M0-M2 because we would like to check the effect of dry deposition and vertical dilution on the OVOCs simulation separately.

- (4) I think the interpretation of the simulation error for acetone is problematic. A more reasonable explanation for the observed small change is that in situ secondary production of acetone is relative unimportant relative to transport in Beijing. The box model set up is such that the effect of secondary production is overestimated (probably due to the specified dilution effect). Could the same be said of the other OVOC simulations? I wonder.

Response: Accepted. The sentence in Section 4.4 has been modified to "The change (12%) of secondary production of acetone estimated by the model is relatively less important compared to transport in Beijing."

The box model did over-predict the absolute concentrations of OVOCs due to inappropriate estimation of atmospheric physical processes (e.g. dry deposition, dilution, transport) and uptake by aerosols. By treating with more caution on abovementioned processes, box model can provide reasonable explanations of OH radical chemistry and secondary production at least for CH₃CHO, MVK+MACR and MEK.

- (5) I do not think that the statement " : : during the full control period, the emission ratios of reactive hydrocarbons attributed to vehicular emissions did not present obvious difference." (in the abstract) is supported by the analysis results. The uncertainties of the emission ratio estimates are too large to state that the emission ratios did not change. It's more proper to state that the emission ratios did not change within 50% or so.

Response: Accepted. The sentence in the abstract may cause some misleading. In

Section 3.3, the traffic-related NMHCs including most of alkenes, acetylene, benzene, toluene and ethylbenzene, the difference of the ERs between 2005 and 2008 ranged from $\pm 6.5\%$ to $\pm 29\%$, within the range of combined error (30%) for ER calculations. So, the sentence in the revised abstract was modified to "...the emission ratios of reactive alkenes and aromatics closely related to automobile source didn't present much difference ($<30\%$)."

More detailed comments

(1) P. 26132, Line 5, change "dramatically" to dramatic.

Response: Accepted and corrected.

(2) P. 26138, Line 2-4. Specified dry deposition rates and boundary layer heights for all model simulations should be stated here. As I indicated earlier, dry deposition rates in M2 and the observed diurnal varying boundary layer height should be used in all simulations.

Response: Thanks for the reviewer's advice, but the dry deposition velocities and boundary layer height (BLH) in M0 are a basic setup for a box model which is also used in some previous studies (Li et al., 2014; Lu et al., 2013; Lu et al., 2012). As above mentioned, we didn't merge M0-M2 because we would like to investigate the effect of dry deposition, boundary layer variation and vertical dilution on the OVOCs simulation separately. To determine changes of OVOCs responding to the control measures, we used the same dry deposition, BLH, vertical dilution, aerosol uptake and primary emission in the two simulations.

(3) Figure 1, please add hourly standard deviations on the figure, so we can see if the difference from emission control is significant.

Response: Accepted. The standard deviations have been added on Fig.1 in revised manuscript.

(4) Figure 1, the diurnal cycle of observed isoprene does not suggest that it is all from biogenic sources (which is assumed in the paper). The decrease after sunset to mid night followed by a constant level from midnight to sunrise and a large increase during morning traffic hours would suggest anthropogenic emissions. Is there strong evidence that isoprene in Beijing is all anthropogenic?

Response: We generally agree with the reviewer's opinion about possible sources of

isoprene.

As mentioned in Section 3.2, isoprene concentrations in the daytime followed the solar radiation and temperature cycles as expected, which reflects the characteristic of biogenic emissions. It needs to notice that the large increase after sunrise should be mostly related to increased temperature and light intensity during that time period. Let's say, even if its increase in the morning was due to morning traffic, it can't explain why isoprene seemed to be affected less by rush hours in the late afternoon (18:00-20:00), when evening peaks occurred for C8-C9 aromatics. However, it doesn't mean that isoprene was all from biogenic sources. In the manuscript P.26140 Line 13-14, there is a sentence saying that "In addition, their low concentrations at night likely indicate small local emissions from vehicles near the site.", indicating that we were thinking of anthropogenic source for isoprene at night.

Another possible reason that caused the constant "isoprene" level during the night was due to the measurement artifact of PTR-QMS on isoprene. The comparison results in Section 2.1.1 (P. 26135 Line 9-13) showed that the isoprene measured by PTR-MS was systematically higher than that measured by GC-MS, particularly for data points with low concentrations (<1ppb). Signal at m/z 69 detected by PTR-MS is recognized as "isoprene signal", but it is also interfered by some fragments from other anthropogenic compounds, such as pentanal, methyl butanal, pentenol (de Gouw et al., 2003), and cycloalkanes (Yuan et al., 2014). That's to say, the measurements by PTR-MS would be provide an additional background for isoprene, and the background can't be ignored in anthropogenic sources dominated areas. That's the reason why we were using isoprene data measured by GC-MS in the following model calculations. Unfortunately, NMHCs measurements by online GC-MS were not available before the control. So, we have to use the PTR-MS results to check the observed changes between uncontrolled and controlled period, as shown in Fig. 1. and in the neutral network analysis.

(5) P. 26141, Line 15, change "provide" to provides.

Response: Accepted and corrected.

(6) P. 26142, why is the effect of dilution neglected in equations (1) and (2)? What are the uncertainties associated with this assumption.

Response: Yes, the assumption in Eq. (2) that the effects of mixing of air masses with different ages is ignored. The limitations of using hydrocarbon ratios (or VOCs relative to a reference compound) to estimate the photochemical age in Eq. (2) by mixing of air masses were point out in previous studies (McKeen and Liu,

1993;McKeen et al., 1996;Ehhalt et al., 1998). Warneke et al. (2007) discussed the influence of an error in estimation of photochemical age on subsequent ER calculations, they estimated the error in the emission ratios to be about 30%, in which 15% from the measurement uncertainty of VOCs and additional 15% from the determination of the initial ratio. Besides the mixing of air masses, de Gouw et al. (2005) reported that the Cl radical chemistry can also affect the photochemical age based on T/B ratios, the inferred photochemical age would be overestimated by about 30% at an average Cl concentration of 10^4 molecules cm^{-3} .

The discussion about the uncertainties has been added in the revised manuscript.

(7) P. 26142, Line 25-27, this statement is too strong when the estimate uncertainty is 30%. I do not know how the uncertainty of 30% is estimated. In addition to the assumptions that went into equations (1) and (2), the fitting errors should also be included. In Figure 4b, for example, the fitting error (of the intercept) looks quite large, much larger than 5-10% due to the assumption of a constant CO background discussed in line 9 of P. 26143. These errors need to be discussed somewhere in the paper.

Response: As discussed in Warneke et al. (2007), an error in the photochemical age results in a small error for the emission ratios. Thus, the uncertainty of emission ratio arises from the uncertainty of (1) measured benzene and toluene, and (2) the determination of initial T/B in equation (2). Varying OH concentration had no effect on the resulting emission ratios. The total ER error was then calculated conservatively by linear addition of the above two errors. For PTR-MS or GC-MS, the measurement uncertainty of benzene and toluene is about 10-15%. As for the uncertainty of the selection of initial ratios, for example, the initial T/B ratios for vehicle exhaust also varied with different fuel composition and vehicle type. That's to say that the error from selecting initial ratios can be regarded as the uncertainty of source profile, which is usually 15-20%. So, the total uncertainty of ER estimation is around 30%.

As for the fitting error that the reviewer mentioned, actually it is dependent on estimation of photochemical age and measurements of VOCs and CO (the x and y axis on Fig.4). The more accurate photochemical age and measured trace gases are, the less scattered data points would occur on Fig.4, and then the fitting error would be getting smaller. So, the fitting error is not an independent factor to determine the uncertainty of emission ratio.

We accepted the suggestion of the reviewer and added the discussion of uncertainty of ERs in the revised manuscript.

(8) P. 26144, Line 22-23, where is the equation? It's not in Table 2.

Response: Sorry for misleading. It was corrected to “Table 3” in the revised manuscript.

(9) P. 26145, Line 4. Is the nighttime OH from the empirical OH-J(D1D) calculation essentially the intercept of a fitting? The statement is unclear.

Response: As described in Rohrer and Berresheim (2006), the intercept of the empirical OH-J(D¹D) relation includes all processes that are light-independent, OH production at nighttime is one of the examples of those processes. That sentence in P. 26145 has been rephrased in the revised manuscript.

(10)P. 26145, Line 26-28, a 50% sink of aldehydes to aerosols seems very large. Was there any measurement of the sticking coefficient? Is it really possible with the observed aerosol surface area in Beijing? I would guess that there is enough ammonia in Beijing that the average acidity of aerosols is close to neutral. Are there measurements for high aerosol acidity in Beijing during the Olympics Games?

Response: Thanks for the suggestion. We’ve checked the aerosol data from AMS and SMPS measurements in the summer of 2008, and found that for most of campaign the average acidity of aerosols was close to neutral due to high ammonia in Beijing (as the reviewer estimated). However, for several days (such as 31 July, 1 August, 11 August and 14 August) the averaged H_{aer}^+ in the daytime was up to 0.01448 mol/L (corresponding to a pH value of 1.84), which indicates high aerosol acidity occasionally occurred during the campaign. As reported in Jayne et al. (1996), a large uptake of formaldehyde by aqueous surface at low temperature and high aerosol acidity. Some lab experiments (Li et al., 2011) and field studies also showed loss of HCHO on aerosols are possible and driven by the liquid water content of the aerosol phase (Toda et al., 2014).

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.

(11)Section 4.2, Figure 6. Please explain in the paper why the simulated peak of acetaldehyde leads those of HCHO and MVK+MACR by 3 hours in the model.

Response: As discussed in Section 4.3, isoprene is the major precursor of HCHO and MVK+MACR, the formation paths of HCHO and MVK+MACR are similar. While,

the photo-oxidation of reactive C3-C5 alkenes contributes most to acetaldehyde production, the different formation path and reaction rate of acetaldehyde formation might lead to different peak time.

(12)P. 26146, Line 8. What fraction of MVK+MACR is due to nocturnal production? Is it significant?

Response: Sorry for the inappropriate statement. There is no significant production for MVK+MACR during the nighttime. Actually, it should be “nocturnal sinks” instead of “nocturnal production” in P. 26146 Line 8. The over-predicted MVK+MACR in the afternoon might be due to unexpected high deposition by vegetation at that time, details in our response to the 5th specific comment from the reviewer#1. And the explanation for modelled peak of MVK+MACR in the afternoon has been added in the revised manuscript.

(13)P. 26147, Line 21-23. The acetaldehyde production is mostly from alkene oxidation. Please look at literature to verify that it has been seen in Beijing or other major cities in China before.

Response: According to the analysis by Sommariva et al. (2011) , on average nearly half (40-50%) of acetaldehyde in urban plumes in the northeastern U.S. is formed via the reaction of the $C_2H_5O_2$ peroxy radical, ethane is a major precursor of this peroxy radical with the percentage of 14-25%. However, when VOCs just emitted from the sources especially in the first two days, propene and other alkenes significantly contributed to the formation of acetaldehyde through the reaction of *HYPPOPO* alkoxy radical, their contribution to acetaldehyde formation is most important (up to 25%). The role of C3-C5 alkenes decreases very quickly because of their high reactivity.

Compared with urban plumes in U.S., the air masses in Beijing are more fresh and close to the emissions. From Fig.4, we can see that the photochemical ages of air masses during the campaign are mostly smaller than 40 hr, within two days. So, in this case, alkene oxidations become important, which is consistent with results in Sommariva et al. (2011).

(14)P. 26141, Line 17-18. Change the word “stable”. Is this result from another study?

Response: Do you mean on the P. 26151, L17-18? The word has been changed to “similar” in that sentence. From the discussion in Section 3.3, the ERs of hydrocarbons associated with vehicle emissions (acetylene, ethylene, propene, benzene and toluene) in Beijing generally agree with those in two US cities,

indicating a similar emission pattern of automobile sources.

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