

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 quantified 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.

References

- de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, *J Geophys Res-Atmos*, 108(D21), 4682, doi:10.1029/2003JD003863, 2003.
- de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *J Geophys Res-Atmos*, 110, D16305, doi:10.1029/2004JD005623, 2005.
- Ehhalt, D. H., Rohrer, F., Wahner, A., Prather, M. J., and Blake, D. R.: On the use of hydrocarbons for the determination of tropospheric OH concentrations, *J Geophys Res-Atmos*, 103, 18981-18997, 1998.
- Jayne, J. T., Worsnop, D. R., Kolb, C. E., Swartz, E., and Davidovits, P.: Uptake of gas-phase formaldehyde by aqueous acid surfaces, *Journal of Physical Chemistry*, 100, 8015-8022, doi:10.1021/jp953196b, 1996.
- Li, X., Rohrer, F., Brauers, T., Hofzumahaus, A., Lu, K., Shao, M., Zhang, Y. H., and Wahner, A.: Modeling of HCHO and CHOCHO at a semi-rural site in southern China during the PRIDE-PRD2006 campaign, *Atmos. Chem. Phys.*, 14, 12291-12305, doi:10.5194/acp-14-12291-2014, 2014.
- Li, Z., Schwier, A. N., Sareen, N., and McNeill, V. F.: Reactive processing of formaldehyde and acetaldehyde in aqueous aerosol mimics: surface tension depression and secondary organic products, *Atmos Chem Phys*, 11, 11617-11629, doi:10.5194/acp-11-11617-2011, 2011.
- Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C. C., Häßeler, R., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S. R., Nehr, S., Shao, M., Zeng, L. M., Wahner, A., Zhang, Y. H., and Hofzumahaus, A.: Observation and modelling of OH and HO₂ concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere, *Atmos Chem Phys*, 12, 1541-1569, doi:10.5194/acp-12-1541-2012, 2012.
- Lu, K. D., Hofzumahaus, A., Holland, F., Bohn, B., Brauers, T., Fuchs, H., Hu, M., Haseler, R., Kita, K., Kondo, Y., Li, X., Lou, S. R., Oebel, A., Shao, M., Zeng, L. M., Wahner, A., Zhu, T., Zhang, Y. H., and Rohrer, F.: Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO₂ concentrations in summer 2006, *Atmos Chem Phys*, 13, 1057-1080, doi:10.5194/acp-13-1057-2013, 2013.
- McKeen, S. A., and Liu, S. C.: Hydrocarbon ratios and photochemical history of air masses, *Geophys Res Lett*, 20, 2363-2366, 1993.
- McKeen, S. A., Liu, S. C., Hsie, E. Y., Lin, X., Bradshaw, J. D., Smyth, S., Gregory, G. L., and Blake, D. R.: Hydrocarbon ratios during PEM-WEST A: A model perspective, *J Geophys Res-Atmos*,

101, 2087-2109, 1996.

- Rohrer, F., and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, *Nature*, 442, 184-187, doi:10.1038/nature04924, 2006.
- Sommariva, R., de Gouw, J. A., Trainer, M., Atlas, E., Goldan, P. D., Kuster, W. C., Warneke, C., and Fehsenfeld, F. C.: Emissions and photochemistry of oxygenated VOCs in urban plumes in the Northeastern United States, *Atmos Chem Phys*, 11, 7081-7096, doi:10.5194/acp-11-7081-2011, 2011.
- Toda, K., Yunoki, S., Yanaga, A., Takeuchi, M., Ohira, S.-I., and Dasgupta, P. K.: Formaldehyde Content of Atmospheric Aerosol, *Environ Sci Technol*, 48, 6636-6643, doi:10.1021/es500590e, 2014.
- Warneke, C., McKeen, S. A., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Holloway, J. S., Williams, E. J., Lerner, B. M., Parrish, D. D., Trainer, M., Fehsenfeld, F. C., Kato, S., Atlas, E. L., Baker, A., and Blake, D. R.: Determination of urban volatile organic compound emission ratios and comparison with an emissions database, *J Geophys Res-Atmos*, 112, D10S47, doi:10.1029/2006JD007930, 2007.
- Yuan, B., Warneke, C., Shao, M., and de Gouw, J. A.: Interpretation of volatile organic compound measurements by proton-transfer-reaction mass spectrometry over the deepwater horizon oil spill, *Int J Mass Spectrom*, 358, 43-48, doi:DOI 10.1016/j.ijms.2013.11.006, 2014.