

Reviewer 2

- **This paper presents a detailed model study of photochemistry in Beijing during the summer of 2007. The authors present a number of potentially important findings regarding the role of oxygenated and aromatic VOC in the formation of peroxy radicals and ozone. Without doubt, there are few studies in that region, so it could be an interesting addition to the literature. I have however several major concerns about the methodology and I think there are some serious flaws in the study, which I outline below; therefore I do not recommend publication at the present moment.**

We thank the reviewer for the review and comments. We are unaware of previous studies of detailed primary radical sources, sinks, and budgets and their implications ozone production based on comprehensive measurements in Beijing, which is the main science contribution of this paper. We feel quite a number of the flaws discussed by the reviewer were due to some misunderstanding of standard modeling practices. As in all scientific methods, there are potential problems. However, some of the issues pointed out by the reviewer are not really problems with the modeling method. The criticism on HONO measurements to be “a unfounded estimates and assumptions for its measurement” seems to be rather harsh and unjustified. The HONO measurement method was documented and previous measurements using this method by the same research group were published by peer-reviewed journals, which we have cited. The reviewer did not provide the reasons for such a statement in the review.

We explain the modeling specifics in the response, which will also serve the readers who are unfamiliar with 1-D/0-D modeling as well. For the reviewer’s concerns that we did not explain well in the initial submission, they are corrected in the revision.

Major Issues:

- **the use of a 1-D model in this context is highly problematic. The authors say that the model was constrained to the observations, which were presumably made at ground level. What happens to the unmeasured species, which are calculated by the model? I would assume they can be transported upwards or downwards along the model column. How this can bias the calculations and the conclusions of the paper is unclear. If the precursors and the sinks of RO_x can be transported along the model column, this should have a significant impact on the calculated RO_x levels. As there is no way to check the correctness of the RO_x calculation (see below) the use of a 1-D model introduces a major uncertainty in the whole analysis.**

Response

This statement has no scientific basis. 1-D modeling’s diffusion transport is based on simulations that do have uncertainty, but it allows explicit simulation of vertical exchange (constrained by

surface observations) and dry deposition. The alternative 0-D modeling would ignore vertical exchange and estimate a chemical lifetime for dry deposition. Hiding the errors does not make the 0-D modeling better than the 1-D modeling. In the 1-D model, the unmeasured species (calculated by the model based on surface observations – so they are constrained) will indeed have a larger reservoir because of mixing in the boundary layer than 0-D model, which is actually what happens in the atmosphere. For short-lived species, the difference between 0-D and 1-D models is usually small. However, we do have found that vertical transport has notable effect on chemical budgets near the surface, as noted in the text (Lines 124 - 126) for PAN (Liu et al., 2010). A comparison of the 1-D model and 0-D model results suggest that vertical transport is important (50%) in contributing to PAN measured near the surface (Liu et al., 2010) and also has impact (<20%) on ROx levels near the surface. Given the importance of vertical transport and dry deposition in regulating chemical concentrations near the surface, a 1-D model is more suitable for analyzing chemical budgets than a 0-D model, which is not capable of simulating either of them. 1-D models with the similar setup have been deployed by previous studies over U.S. (e.g. Trainer, M., et al. (1991), Observations and Modeling of the Reactive Nitrogen Photochemistry at a Rural Site, J. Geophys. Res., 96(D2), 3045–3063).

We agree that observations of OH, HO₂ and RO₂ and further a more comprehensive set of chemical compounds such as other OVOC compounds would be a quite useful addition to the study. Unfortunately, such data are not available. We wrote in the introduction:

“Given the difficulty of interpreting empirical evidence, another approach is through in-depth observation-based chemical budget analyses to gain insight into the chemical system. In this work, we analyze the O₃ photochemical processes in Beijing in August 2007 during the CAREBeijing (Campaigns of Air quality REsearch in Beijing) Experiment employing the 1-D version of the Regional chEmical and trAnsport Model (REAM-1D) constrained by observed chemical species and physical parameters, including O₃, NO, PAN, HONO, VOCs, and aerosol surface areas. The goal is to gain a detailed understanding of the budgets of ROx (OH + HO₂ + organic peroxy radicals (RO₂)) radicals and formation processes of O₃ and to understand the implications on emission control strategies in Beijing and other polluted regions in China.”

- **ROx were not measured, so the only way to assess how good the model calculation is, would be to see how well SAPRC performed in other studies. However, it appears that the authors have modified the aromatics scheme, making it difficult to compare the reliability of their mechanism with that of SAPRC. In any case, this question is not addressed at all, nor the uncertainty of the model discussed in any way. Since a major part of the paper consists in using calculated ROx, this is a major deficiency.**

Response

The aromatics chemical scheme was taken from SAPRC-07. Modeling is an important tool for atmospheric chemistry analysis and air quality applications. The chemistry scheme used in

modeling does have uncertainties. The fact that there are uncertainties and no measurements for RO_x does not suggest that atmospheric modeling is useless for analysis and applications. The RO_x budgets we calculated and described underlie all oxidant chemistry modeling calculations, 0-D, 1-D, or 3-D. Examining the details of the RO_x budget is the first step to document the model sensitivities and understand the model results, which is what we did in this paper.

The original chemical mechanism used our model (now used in GEOS-Chem) was initially developed for 0-D model studies of tropospheric radical chemistry on the basis of atmospheric measurements (e.g, Jacob et al, (1987) for ABLE-2A, Jacob et al. (1992) for ABLE-3B, Jacob et al, (1996) for TRACE-A, Jaegle et al. (1998) for SONEX, and Schultz et al. (2001) for PEM-Tropics A). Many field experiments (ABLE-3B, TRACE-A, SONX, PEM-Tropics A) sampled polluted biomass burning or fossil fuel combustion outflows. These previous studies showed that the mechanism is suitable for analysis of those measurements. These studies also showed that the mechanism makes good use of chemical species that can be directly measured. This is critically important for analyze measurement data collected from field experiments. SPARC type of mechanism is in principle similar to what we used.

Furthermore, the 1-D model is the 1-D version of our REAM model. The 3-D REAM model has been successfully applied in simulating regional pollution chemistry over the U.S., as well as over China. The chemical mechanism has been shown working very well in simulating O_3 , PAN, and other chemical species (e.g. refs in the text, Lines 103 - 105). In addition, we also conducted comparison of several chemical mechanisms, including REAM (GEOS-CHEM), SAPRC-99, SAPRC-07, RACM, before the expansion with chemistry aromatics) with respect to the VOC species measured during the CAREBEIJING experiment. We found that the mechanism used in REAM (also in GEOS-Chem) and other mechanisms, including SAPRC-99, SAPRC-07, and RACM, are similar in representing NO_x -VOC- O_3 chemistry, with some differences in the lumping of VOC groups. The mechanism in REAM has the most explicit free radical reactions; SAPRC-07 is the one with the most up-to-date knowledge of aromatics chemistry (product yields last updated in 2009) and is also the most compatible with the mechanism in REAM (e.g. the similar representation of free radicals). Therefore, we chose SAPRC-07 as the reference to do the expansion of aromatics chemistry. Furthermore, we also conducted sensitivity tests with aromatics reactions in SAPRC-07 and RACM and we found that the simulated PAN concentrations agree to within 10%.

References mentioned:

Jacob, D. J., and S. C. Wofsy, Photochemistry of biogenic emissions over the Amazon forest, *J. Geophys. Res.*, 93, 1477-1486, 1988.

Jacob, D.J. et al., Summertime photochemistry at high northern latitudes, *J. Geophys. Res.*, 97, 16421-16431, 1992.

Jacob, D.J. et al., Origin of ozone and NO_x in the tropical troposphere: a photochemical analysis of aircraft observations over the South Atlantic Basin, J. Geophys. Res., 101, 24,235-24,350, 1996.

Jaegle, L. et al., Origin of NO_x in the upper troposphere over the central United States, Geophys. Res. Lett., 25, 1709-1712, 1998.

Schultz, M. et al., On the origin of tropospheric ozone and NO_x over the tropical Pacific, J. Geophys. Res.104, 5829-5844, 1999.

- **a significant part of the paper is dedicated to HO₂ interaction with aerosol. First, aerosol measurements are not mentioned, so it is not clear where the surface area is coming from. Second, the reason given for the choice of gamma (page 4685) does not make any sense.**

Response

The instrument for aerosol number distribution measurement has been added (Lines 95-97: “*Size distributions of aerosols (3nm - 10μm) measured every 10 minutes with a Twin Differential Mobility Particle Sizer -Aerodynamic Particle Sizer (TDMPS-APS) were used to calculate aerosol surface areas.*”). The choice of maximum $\gamma = 0.2$ is based on the recommendation by Jacob (2000). Although $\gamma = 0.02$ is chosen to be used the standard model based on performance of PAN simulation, we do recognize the uncertainty in γ and that is why we conducted sensitivity simulations by varying γ from 0 to 0.2 (Section 3.3.3)

- **a potentially important finding is the role of HONO. It appears that the model generates HONO based on a "fake" reaction converting NO₂. This is not, per se, a problem but several things should be discussed: 1) how good was the HONO measurement 2) has this source any relation with laboratory or field studies of heterogenous formation of HONO 3) is this source consistent with the aerosol measurements (if any) and the total nitrogen data? The only comment on the reliability of HONO measurements is on page 4691, where the authors make the bold statement that because the HONO concentrations are so much higher than in other places the instrument uncertainty are likely lower (!) I don't think the authors can draw the conclusion that HONO plays such a major role under these conditions, based on a unfounded estimates and assumptions for its measurement and formation process. The authors state that HONO is an ozone loss term in the sense that consumes NO₂; however, it is also a source in the sense that produces NO which forms NO₂. Has this feedback being considered?**

Response

The HONO measurement is described in detail in the supplement with references. The statement about the HONO measurements mentioned by the reviewer (Lines 305-309) is meant to state the fact that the high HONO concentrations that are much higher than the detection limit (a few hundreds of pptv, as shown in this and other studies over China) suffer much less from the measurement error than those measurements that are close to the detection limit (tens of pptv), which is a major challenge faced by most daytime HONO measurements (e.g. Pinto et al., 2010) in other regions. In the same paragraph, we mentioned a number of other studies showing high HONO mixing ratios similar to what we reported in Beijing. We note here that these HONO measurements were not from the same research group.

The pseudo NO₂-HONO conversion is capable of reproducing the observed HONO. The possible mechanism of the HONO source in this paper is not within the scope of the present paper and will be addressed elsewhere. We noted in the paper that such a large daytime HONO source is apparently prevalent over China and unique compared to other regions (please see the cited references); the nature of this missing HONO source is under discussion (Lines 210 - 216). Understanding the possible relationship between HONO and aerosols and/or other factors, based on laboratory studies will be the focus of a future paper.

NO-to-NO₂ conversion via $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2$ does not result in O₃ production. NO+HO₂ (or RO₂) reaction produces ozone, but it's a minor branch compared to O₃ reaction. Therefore photolysis of HONO leads to O₃ loss. The reviewer could use $\text{O}_x = \text{O}_3 + \text{NO}_2$ to look at the production and loss from the reactions in question.

- **I think there is a serious methodological mistake in sections 3.2 and 3.4. The authors use the model to calculate ozone production and then change the model parameters to observe the sensitivity of ozone production. Given that the model is constrained to ozone and NO_x observations, it does not make sense to use it to calculate the formation of ozone. What the authors are doing in this case is equivalent to use the answer to obtain a question which is already known; only a model unconstrained to ozone may be used to calculate ozone formation and loss. This, without considering the complications introduced by the use of a constrained 1-D model. Also, I would be extremely careful in drawing conclusions on the VOC-limited or NO_x-limited regime, based on the correlation of the model results with some empirical diagnostic equations. First of all, it defies the purpose of using a model. Second, it is, at best, highly uncertain, and, at worst, a wild guess. In any case the reliability of these equations should be debated thoroughly.**

Response

The reviewer does not appear to understand how model diagnosis of ozone budget is done (please see the 0-D model studies that we cited earlier and the references therein). Many early atmospheric chemistry papers starting from 1970s used the budget analysis to understand

tropospheric ozone in this manner. The diagnostic equations are published by peer-reviewed journals and cannot be just ignored because of personal preference.

Calculating O₃ production/loss rates based on observed NO and calculated HO₂ and RO₂ concentrations is essentially a diagnostic analysis, in which O₃ acts as a source of OH and affects HO₂/RO₂ indirectly. Fixing O₃ to observations is only intended to precisely representing this radical source. The possible effect due to the fixed O₃ on the sensitivity results is not expected to be large because O₃ is shown not to be a large radical source; therefore O₃ changes will not cause substantially different chemical behaviors and responses.

Our conclusion of the chemical regime does not rely on the diagnostic equations, which, we agree, are subject to uncertainties and assumptions. Both sensitivity simulations (Section 3.4.1) and diagnostic equations (3.4.2) are used for this purpose, and they are shown to agree in suggesting a transition regime. Our intention of using these equations is only to approach the problem from another angle and perform a test of these equations.

- Minor Issues:

- in sec. 2.1, three instruments to measure VOC are mentioned, although the authors don't say which species the GC/MS/FID measured. Were C2 VOC measured? And CH4? Which oVOC?

Response

The VOC measurements are described in detail in the supplement. All the answers to the reviewer's questions are there.

- the authors say that the model was run with a 1 min timestep. Since the VOC measurements have a 30 min frequency, the authors should say whether they were interpolated to 1 min and if so how and how it could impact the results.

Response

To clarify this, we have added statements in the method section (Lines 118 -122) that read "*For measurements made with a time resolution longer than 1 minute (e.g. NMHCs and OVOCs, aerosol surface areas), constant measured values were assigned during the measurement period. Missing data points on some days due to instrumental issues were replaced with the corresponding value in the overall average diurnal profile at the time of missing data.*"

- how are the production/loss rates calculated? are these reaction rates (eg, k[HO₂][NO]) or pseudo-first order rates (eg, k[NO])? it is very different.

Response

These are reaction rates calculated in the model using concentrations of NO, HO₂ and the rate constant for NO+HO₂ ($k = 3.50E-12 \exp(250/T)$). There is no reason to use a pseudo first order rate in photochemical modeling.

- section 3.1.2: the last paragraph is not clear: either it is stating the obvious or it does not make any sense.

Response

This paragraph is modified as follows (Lines 245-252):

“Another feature in the chemical system in Figure 2 is the coupling of NO_x and VOCs chemistry and the comparable importance of their roles as RO_x sources and sinks. Both NO_x and VOCs are involved in major RO_x primary sources, i.e. the source OH from excess HONO (2.2 ppbv h⁻¹) and photolysis of OVOCs (4.2 ppbv h⁻¹). Both of them are also involved in RO_x sinks through organic nitrates. This feature of chemistry could have implications for O₃ sensitivities to NO_x and VOCs (Farmer et al., 2011). In Section 3.2 – 3.3, we examine the formation of O₃, and its sensitivities to various factors, including excess HONO, aromatics, γ (HO₂), as well as NO_x and VOCs.”

- the style and quality of the paper is mixed, with some parts in decent English and some in really bad English.

Response

The writing of a paper could always be further improved. We have revised the paper as well as we can.