

Reviewer 1

This paper uses data obtained during August 2007 over Beijing (CAREBeijing-2007) and a 1-D photochemical model to examine the budgets of ROx radicals and O3 production. Major findings are that photolysis of OVOCs is largest primary source of ROx, and that photolysis of HONO is a predominant primary source of OH (with HONO largely from a parameterized NO2 heterogeneous reaction source). It was determined that aromatics were the largest contributor to OVOCs over the Beijing region, and that O3 production is in the transition between NOx and VOC limited. I thought this paper was quite interesting, with some intriguing findings (e.g., aromatics largest source of OVOCs, and thus ROx). However I had several questions remaining after reading the paper which need to be discussed in more detail. I recommend publication after revision.

We thank the reviewer's constructive comments. We respond to the comments one by one as follows and have made revisions accordingly.

General comments follow:

(1) Comparison to results/conclusions from CAREBeijing-2006 would be useful for context (e.g., Lu et al. 2010, Oxidant (O3+NO2) production processes and formation regimes in Beijing, JGR, 115, D07303, 2010)

Response:

We agree. We actually have done such comparison in the text (Section 3.2.1, Line 259) regarding the ozone production rates, which is the focus of the study by Lu et al. (2010). We have added another comparison as follows: (Line 298-299) "*Similar amplifying effect by HONO on P(O₃) was also noted by Lu et al. (2010).*"

(2) Description of Model: The description of the model and how it was used should be expanded. The model was constrained to surface observations – however, it is not clear whether the model was constrained by a repeating 24-hour average cycle, or by the full time series of data over the 30 day period. I am also not clear why a 1-D model was necessary for this study – the full utility of the 1-D model was not discussed in conjunction with the results. The paper describes that vertical transport is driven by WRF assimilated met fields based on the NCEP reanalysis, but any role for vertical redistribution is not discussed in the results. What concentrations were used to initialize or constrain the upper levels of the 1-D model, and how did vertical transport affect the results? How were values such as temperature, water vapor, and photolysis rates determined in the model? Were these also constrained to observation, or were they obtained from a 3-D model run?

The largest RO_x source was shown to be photolysis of OVOCs – were these rates calculated using clear sky model assumptions for the photolysis rates, or was there an adjustment for reduction in irradiance due to cloudiness and the considerable aerosol cover?

Response

The 1-D model has advantages over 0-D model in (1) resolving vertical transport process that has been shown to be important for chemical budget (e.g. for PAN) near the surface in Beijing (Liu et al., 2010); (2) explicitly simulating dry deposition rates, which is assumed or estimated in a 0-D model.

We agree that a 1-D model could be further utilized to analyze chemistry and transport not only near the surface but also in the boundary layer. Due to the lack of observational constraints on upper model layers, in the initial submission we chose to focus on discussing model results at the surface layer. In the revised version, we have added a paragraph (Lines 394-405) and two additional figures (Figure S1 and S2) in the supplement to address the vertical distribution of O₃ production and chemical regimes in the boundary layer. The abstract and the conclusion have also been changed correspondingly.

Physical parameters (i.e. water vapor concentrations, temperature, clouds) that are needed in chemical module are taken from WRF output, and photolysis rates are calculated using the Fast-J scheme taking into account the cloud effect.

According to the reviewer's suggestion to expand the model description, we have revised Section 2.2 as follows (Lines 111-144):

“Meteorological parameters (i.e. water vapor concentrations, temperature, pressure, and diffusion coefficient) in the model are taken from WRF results. Photolysis rates are dependent on cloud fraction and optical depth calculated based on WRF meteorological fields (Choi et al., 2008b).

The standard 1-D model is constrained with measured CO, O₃, NO, HONO, NMHCs (C₂–C₉), OVOCs (acetone, acetaldehyde and formaldehyde) and aerosol surface areas in the first layer. 3-D REAM model simulated chemical tracer concentrations (Zhao et al., 2010) in the column over Beijing were used as initial and boundary conditions at upper model layers. 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. The 1-D model was run with a 1-minute time step, continuously from 1 August to 30 August 2007 and the results for the last 20 days were analyzed after a spin-up time of 10 days. The REAM-1D model with such a setup is able to reproduce the observed PAN near the surface in Beijing, which has been shown to be contributed equally by chemistry near surface and downward vertical transport (Liu et al., 2010). In addition to resolving vertical mixing in the boundary layer, the 1-

D model allows for explicit computation of dry deposition rates, which are assumed or estimated as lifetime parameters in box models. For additional information of the REAM-1D model and its performance, we refer the readers to the supplement and Liu et al. (2010).

In order to investigate the sensitivities of RO_x budget and O₃ production to OVOC and HONO, both of which have photochemical sources and sinks, OVOC and HONO cannot be specified in the model using observed values. Model simulated OVOCs, including formaldehyde, acetaldehyde, and acetone, methylglyoxal, and glyoxal, agree with the observations within 20% in terms of daytime average concentrations (Table S3 in the supplement), indicating that secondary production is their predominant source. Removing the constraint of observed OVOCs in the standard model did not lead to notable changes in RO_x concentrations or O₃ production/loss rates. Exceptionally high level of HONO was observed at daytime (~1ppbv in the afternoon) during the study period. The gas-phase source from the NO+OH reaction alone could only explain a small portion (~10%) of the observed HONO concentrations. We therefore introduced a pseudo-reaction of NO₂ → HONO in the model (at a rate of about 6.4 x 10⁻⁵ s⁻¹ on average during daytime) to reproduce the observed daytime HONO and quantitatively estimate the primary radical source from the heterogeneous HONO production pathway. Replacing the observed HONO with the pseudo HONO production does not lead to notable changes in RO_x concentrations.”

(3) The paper states that major source of OVOC is secondary production (p. 4684, line18-21), and that comes from the finding that when the constraint of measured OVOCs is relaxed (acetone, acetaldehyde, and formaldehyde), predictions are “within 20%” of the observed diurnal average. I would like to see a better breakdown of this; what is the mix of these species and how does the model do predicting the individual species? The lifetime of acetone near the surface is on the order of several weeks, while those of formaldehyde and acetaldehyde are on the order of hours, so the relative mix of these species is highly relevant to the ultimate source of RO_x. In other words, how does the model do predicting the diurnal cycles of the more reactive aldehydes? It seems it would be much more useful to see a daytime/diurnal cycle analysis as opposed to a 24 hour average. Because there are other OVOCs that are clearly important (dicarbonyls from oxidation of aromatics), it would also be useful to see the breakdown between acetone, aldehydes, and dicarbonyls. Continuing on the impact of OVOCs, the discussion of the sensitivity calculations which compute OVOCs includes the impact of the differences on the the RO_x cycling, but I don’t know what the OVOC mix is or the concentration variance in OVOCs for those simulations. It would be useful to know what concentration ranges we are working with for the individual species.

Response

We agree that OVOC concentrations are useful information to provide and that acetone has negligible effect on radical budgets due to its long lifetime. We have added a table in the supplement (Table S3) tabulating daytime average concentrations for formaldehyde, acetaldehyde, methylglyoxal, and glyoxal from the observations and the model (scenarios with and without aromatics). Please also see the changes in the text in the previous response.

Although the diurnal cycles are not shown due to the coarse (3-6 hours) resolution of the measurements and a large number of missing data points, we did find that the model is broadly consistent with the observations showing a noontime peak of these OVOCs. We also have added statements as follows in the text (Lines 318-321):

“Inspection of the model results shows that OVOCs concentrations increase drastically after adding aromatics (e.g. ~100% increase of formaldehyde; ~65% increase of acetaldehyde, a factor of 5 increase of methylglyoxal and a factor of 10 increase of glyoxal (Table S3 in the supplement))”.

(4) NO₂ heterogeneous rate for conversion to HONO: HONO does not seem to be a constraint in the model per se (as is described in the text), but is calculated using a NO₂ heterogeneous conversion such that observations are matched. What is the value of this rate that was determined to be necessary to match HONO? Is that rate reasonable and/or similar to previous estimates (3.5E(-6) s(-1) Elshorbany et al. 2009 or 3.3E(-6) s(-1) Alicke et al. 2002)? The rate you calculate would be a useful addition to the paper.

Response

A NO₂-to-HONO conversion rate around $6.4 \times 10^{-5} \text{ s}^{-1}$ is needed and used in the model to reproduce the daytime HONO (as obtained given the 2.3ppbv h⁻¹ HONO production rate and about 10 ppbv of NO₂ during daytime). The daytime excess HONO production rate here (2.3ppbv h⁻¹) is a bit larger than that in Santiago (1.7ppbv h⁻¹) (Elshorbany et al., 2009). Further, considering NO₂ at Santiago is a factor of 4 higher than Beijing, the NO₂-to-HONO conversion rate at Beijing is actually much higher (by a factor of 4 - 5) than that in Santiago. The reason is still under investigation. We note that the values mentioned by the reviewer in the studies by Elshorbany et al. (2009) and Alicke et al. (2002) are nighttime HONO formation rates and thus not comparable to our daytime rates.

According to the reviewer's suggestion, we have added a statement with the rate provided (Line 141) which reads *“We therefore introduced a pseudo-reaction of NO₂ → HONO in the model (at a rate of about $6.4 \times 10^{-5} \text{ s}^{-1}$ on average during daytime) in order to reproduce the observed daytime HONO”.*

(5) Additional sources of radicals: What role does ozonolysis of alkenes play in the radical production here? What are isoprene levels over Beijing, and does isoprene have any significant impact on OVOCs (formaldehyde)? Is there any possibility for a role for $\text{NO}_2^* + \text{H}_2\text{O}$ radical production? (e.g., Li et al. 2008)

Response

Ozonolysis of alkenes does not play a notable role ($< 0.1 \text{ ppbv h}^{-1}$) in radical production due in large part to the abundance of other sources as stated in the paper. Isoprene is 0.88 ppbv on average during our campaign (as shown in Table S2 in the supplement) and contributes about $\sim 3 \text{ ppbv}$ ($\sim 30\%$) of HCHO in the model. Based on our model calculation, $\text{NO}_2^* + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{OH}$ is not a notable radical source ($< 0.1 \text{ pptv h}^{-1}$) in Beijing, even using the upper limit of rate constant ($1.7 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) for the reaction based on Li et al. (2008). These minor sources are not shown or discussed in the paper due to their negligible contribution to the total radical budget.

We have added a statement in Section 3.1.2 (Line 200) that reads:

“Minor ROx radical sources ($< 0.1 \text{ ppbv h}^{-1}$), e.g. ozonolysis of alkenes, are not shown.”

(6) O₃ production: Does the calculated surface net O₃ production agree with observations of O₃? i.e., does the maximum increase in concentrations correspond to the maximum net production around 11 am local time? What did O₃ production look like at levels above the surface –what are the sensitivities to O₃ production at higher altitudes relative to those at the surface? This is another application of using a 1-D model that was not taken advantage of.

Response

The maximum increase of O₃ concentration is around 11am, corresponding to the maximum net O₃ production near the surface.

To address the comment on O₃ production at higher altitudes, we have added a paragraph (Lines 394-405) and two additional figures (Figure S1 and S2) in the supplement to address the vertical distribution of O₃ production and chemical regimes. The abstract and the conclusion have also been changed correspondingly. Please also see the response to the reviewer’s comment (2).