**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Summertime photochemistry during CAREBeijing-2007: $RO_x budgets and O_3 formation$" by Z. Liu et al.

Anonymous Referee #1

Received and published: 27 March 2012

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. 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)

(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 ROx 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?

(2) The paper states that major source of OVOC is secondary production (p. 4684, line 18-21), 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 ROx. 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 ROx 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.

(3) 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 ($\sim$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.

(4) Additional sources of radicals: What role does ozoneolysis 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 NO2*+H2O radical production? (e.g., Li et al. 2008)

(5) 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 4679, 2012.