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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes" *by* L. K. Xue et al.

Anonymous Referee #1

Received and published: 23 September 2014

General Comments:

This paper presents data on ozone, NOx, VOCs and aerosol distributions from four cities in China that are subject to severe ozone pollution episodes. All data are from the mid 2000's, and thus likely representative of a point in time during the recent industrial and urban growth that has occurred in China.

After summarizing the characteristics of the sites and the data collected at each, the authors present two separate analyses, both based on an MCM box model. They first analyze chemical ozone production rates, the influence of transport, and the contribution of NOx and speciated VOCs to local ozone production at each site. In a separate set of model runs, they examine the sensitivity of local ozone production to

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heterogeneous processes, including N2O5 uptake to produce ClNO2, HO2 uptake to aerosol, and conversion of NO2 to HONO. They demonstrate that for reasonable values of heterogeneous reaction rates, these processes have a non-negligible influence on chemical ozone production rates.

The paper is well written and presents new results relevant to ozone in China and to heterogeneous process chemistry. I recommend publication following attention to the specific comments below.

Specific comments and technical corrections:

Abstract, line 10: “Rural site of Beijing” should be replaced by “Rural site downwind of Beijing”

Abstract, lines 14-15: “VOC-limited” and “NOx-Controlled” regimes. Do the authors mean the same thing by “limited” and “controlled” in this context? If so, recommend using a consistent terminology (either NOx-limited and VOC-limited, or NOx-controlled and VOC-controlled).

Page 20771, line 9: Recommend using the term “neglected” rather than “ignored” since the former does not imply any ill intent.

Page 20773, line 16: “a mountainous region” rather than “mountains regions”

Page 20774, line 3: What is the estimated efficiency of the NOy converter? Was this optimized for NOy, or run as an NO2 instrument and then interpreted as NOy? Similarly, the OBM would have required an input for NOx, not just NO. Was the NO2 calculated from photolysis rates for this purpose? If so, the authors should specify.

Page 20774, last line: Replace “besides” with “In addition”

Page 20775, line 11-12: Here, and in the instrument section above. Were the aerosol size distributions measured under dry or ambient humidity conditions? Were the surface area calculations done for dry aerosol or corrected for relative humidity? Such a

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correction could substantially alter conclusions regarding rates of heterogeneous processes, and requires some further experimental details.

Page 20776 and equations (1) and (2). The authors should state which terms in (E2) are dominant. Likely there are several that are relatively small compared to others.

Figure 4. The calculation of the transport contribution is not straightforward from the figure itself. It would be helpful if the quantity RÂň_meas were plotted on the figure as a line so that that subtraction to determine R_trans could be determined.

Section 3.3.1: The section should perhaps be titled "ClNO2 production" rather than "N2O5 hydrolysis", since the conclusions come from comparison of runs that both include N2O5 uptake, but differ in the amount of ClNO2 produced.

The model approach should be clarified. The ClNO2 is the integral of the locally produced ClNO2 at each site, with no transport term, correct? Thus, the transport effects discussed in the preceding section need to be neglected?

The conclusions are given in the relatively simple form of a percent increase in ozone production rates – these are presumably an average, and not uniform over the course of a day, since the ClNO2 photolysis will occur mainly in the morning? Finally, the authors may wish to comment on the surface titration of nighttime ozone seen in Figure 4 and its influence on ClNO2. Presumably there could be more ClNO2 formed immediately above each of the measurement sites, where ozone does not fall to zero?

Page 20783, equation (4): Why is diffusion limitation accounted for here, but not with respect to N2O5 uptake in equation (3)? If this is simply a consequence of the range of uptake coefficients involved (large for HO2), this should be explicitly stated.

Page 20785, equations 4 and 5. Which term dominates? Ground or aerosol surface? If ground, would the influence on local ozone production depend on vertical gradients in HONO?

Page 20786, line 7-8: Does the heterogeneous production of HONO consume NOx?

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The photolysis should release NO, leading to no net effect on NOx and thus no effect on ozone other than from the OH production.

Page 15, line 26: Justify choice of daytime NO2 uptake coefficient to aerosol? Seems arbitrary relative to the choice made for ground uptake?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 20767, 2014.