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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozone production in four major cities of China: sensitivity to ozone precursors and heterogeneous processes" *by* L. K. Xue et al.

Anonymous Referee #1

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Review of "Ozone production in four major cities of China: sensitivity to ozone precursors and heterogeneous processes" by L. K. Xue et al for Atmospheric Chemistry and Physics

The four cities mentioned in the title are, from an atmospheric point of view, quite interesting. With one possible exception they fall into the megacity category. A master mechanism box model constrained with observations of CO, NO, O3, and VOCs is used to determine O3 production rates and the sensitivity of O3 to NOx and VOCs. Scenarios are considered that include poorly understood heterogeneous processes, namely loss of N2O5 and peroxy radicals and production of HONO. Although I can't

point to ground breaking findings, it is an interesting and nicely crafted study.

One concern is that the data used for the current study is from field campaigns conducted in 2004 to 2006. I know in general terms that there has been increased industrialization in China. Quite likely NOx and VOC emissions have increased. I would expect that ozone sensitivities have changed since anything resembling a proportional increase in NOx and VOCs will make O3 more VOC limited. Another concern is that there have been many publications using these data sets. I see some (inevitable) similarities between this and previous publications but no obvious duplication.

I recommend publication after minor revisions addressing points below.

p 27246, line 2 "A typical and intractable issue is photochemical smog ..." Intractable may be the wrong word. Can the problem not be understood? Is there nothing that can be done about it?

p 27246, line 24 "ozone levels show an increasing trend over the last decade" Please provide an explicit time frame. The papers cited are dated 2006 to 2008. Xu et al (2008) refers to studies done up to 2006. From this I would infer that the last decade is 1996 to 2006. Are there other studies that describe ozone trends in a period ending closer to the present.

p27249, line 3 free from uncertainties due to differences in methodology This thought is said better later on. Uncertainties are minimized. Two identical instruments are not necessarily going to give identical results.

p 27253, line 8 – 16. nine day pre-run used to generate concentrations of unmeasured species. Are there any comparisons that can be made for some intermediate lifetime species such as NO2, HCHO, and H2O2?

p27253 line 6. photolysis frequencies were further scaled with measured solar radiation How was this done? Were there clear sky days that you could use to normalize an actinic flux on a day that was not clear? A straight ratio would still not capture the

different contributions of direct and diffuse radiation to photolysis.

p27253, Eq. 2 There are arguments that can be made for and against including loss of NO2 in Eq. 2. An alternate view is that O3 is lost when emitted NO is converted to NO2.

p27255 line 5-9. discussion of traffic and industrial contributions to diurnal pattern. The CO and NOy traces from TMS and especially CP do not look like local traffic, which is characterized by a morning peak with the highest concentrations of the day, caused by a shallow boundary layer.

p27257 line 4. 286 ppb ozone Please clarify that this is not in Fig. 5a. Was the observation of 286 ppb O3 during the campaign that is analyzed here? I recall reading about it several years ago.

p 27261 Eq 3. k10 includes a term for interfacial mass transfer but not a diffusion term such as in Eq 4. Was the mass transfer term regarded as rate limiting in all circumstances?

p27261 line 20-25. important heterogeneous loss pathway at night Pathway is a large fraction of total loss of O3 at night. However absolute amount of O3 lost at night is small.

Section 3.4 Heterogeneous chemistry. The reader must be given some sense of aerosol concentrations in order to put results in perspective. Loss rates depend on surface area, which must be in model. It would be a service to the reader if you can convert to the more familiar units of volume and size (assuming a single size would be OK).

p27265 line 7 13% enhancement in O3 production. I can't tell from figure where there is a 13% enhancement. Integrated over a day the enhancement appears to be very small.

p27265 line 11. observed daytime HONO concentration up to the ppb level. The figure

shows calculated HONO at ppb level until 09:00, so it is not that different during the time of day when HONO is thought to be an important radical source.

Fig. 5. The red bars sometimes hide the blue bars. This is not a problem except for a sliver of blue below zero in the panel a during the in-situ production time period. A note in the Fig 5 caption would be useful.

The quantification of transported O3 vs. in situ production was of particular interest. Section 3.3.3 ends with an appropriate disclaimer about the lack of universality of model predictions.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 27243, 2013.