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Atmospheric Chemistry and Physics Discussions

Interactive comment on "VOC reactivity and its effect on ozone production during the HaChi summer campaign" *by* L. Ran et al.

Anonymous Referee #1

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Review of "VOC reactivity and its effect on ozone production during the HaChi summer campaign" by L. Ran et al for ACP

Measurements of NOx and VOCs were made in a very polluted region between two mega cities, Beijing and Tianjin. Ozone sensitivity to NOx and VOC changes was calculated with a box model, constrained by observations. Photochemistry reminds me of what was found in Houston, Texas in several field campaigns starting in 2000. Ozone levels were extremely high: "Highest 1-hour ozone was nearly 200 ppb." VOC to NOx ratios were very high with the consequence that "Ozone production is typically limited by NOx under current precursor conditions." This is supported by the data but is it very unusual that ozone production is NOx limited under such highly polluted conditions.

I would like to see better documentation of modeling methods and results. Questions about the calculations are given below. More important are the results contained in Fig. 16 of Chameides et al (1992). That graph shows that conditions from this field campaign (200 ppbc Propy-Equiv and 20 ppbv NOx) give rise to an ozone production rate greater than 100 ppb per hour. Clearly that rate can't be sustained for a long time period without ozone concentrations becoming much larger than indicated in Fig. 7 or in the observations. Measurements are evidently dominated by fresh emissions as indicated by very high concentrations of short lived butenes. If this were Houston, the mix of high NOx and extremely high VOC reactivity would be caused by emissions of light olefins from petrochemical facilities. Here the mixture of VOCs is different. I don't know enough about differences in emissions sources in China and the US to comment.

The authors have made measurements under interesting conditions. I'm not familiar with most of the work done around Beijing so I can't say that conditions were unique. Hundreds of scientists participated in the Houston studies. This is a much smaller effort and it would be unfair to expect results that are anywhere near as comprehensive.

I believe this article should be published with some significant modifications. Some are listed below. The list contains a mix of items that are important and some simple typos. What I would really like to see is an appraisal of how these measurements fit into a broader context – and what to make of the extremely high ozone production rates suggested by Chamedies et al. Perhaps the answer is simple and has to do with how the box model calculations in this paper are carried out. Then the question becomes whether methods are appropriate and what are calculations really saying.

Comments in order of appearance in text: Abstract, line 24-25. "Total VOC reactivity is dominated by anthropogenic VOCs, including aromatics, alkanes, and most alkenes." I don't know what information this sentence is trying to convey.

Section 2.2 NOx measurements, Sec 3.3 line 26-28, and Fig. 2. Measurement should be described here, not later on in Sec. 3.3. Evidently this is a 2 channel machine,

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measuring NO and NOy. I don't know the details of this instrument, but a Mo converter heated to 350 will quantitatively reduce HNO3, organic nitrates, nitrate aerosol, and PAN to NO. In anything but fresh emissions, NOx oxidation products will be greater than NO2. The ratio, NO2/NO appearing in Fig. 2c should by replaced by, for example NO/NOy, or NO/NOy* is there is indeed the converter does not quantitatively reduce NOx oxidation products. An explanation of NOy* would be needed.

Page 4, line 16-18. Why were 4 bags filled for a VOC analysis. Are results always averaged?

Page 5, line 4. It is good to see the factor Cj in the Propy-Equiv(J) formula, because that is how it was defined in Chameides et al. Many people leave it out.

Page 5, line 21 "Six scenarios were arranged.." I don't think that scenario is the best description. The 6 cases represent calculations based on real data from 6 different days. I think of scenario as made-up, as in the variation of NOx concentration.

Page 5, Sec. 2.4 Observation based modeling approach. More information is needed to describe the calculations. Some of my questions:

Were VOCs and NOx held constant at observed or prescribed values during 5 day calculation?

Do initial VOCs represent measured concentrations at some particular time of day?

How was NOx partitioned between NO, NO2, and perhaps other compounds?

Did this partitioning change to follow a diurnal cycle?

Were oxidation products allowed to accumulate? The steady state concentrations of short lived products such as HCHO and CH3CHO will become large and effect O3 production. Less reactive ketones will also build up to large values over 5 days.

Page 6, line 14 "remain averagely" replace with averaged

Page 9, line 4 “far away from the petrochemical facilities near the coastal area” Are these the facilities in the yellow area in Fig. 1? Text implies that they are to the east, which might put them off the right side of map – east of 118 longitude.

Page 10, line 14 1 to 14 ppbv isoprene 14 ppb is a very high concentration, probably close to the maximum reported from biogenic sources. Is there any chance that the high isoprene is from petrochemical facilities? Isoprene is a feedstock.

Page 10, line 29 Measured n-hexane ... Better to say n-hexane is the most abundant species measured ...

Page 12, line 13 -14 underestimate of the overall VOC reactivity .. where only a subset of speciated VOCs are capable of being specified as model inputs My concern is that the direction of error is not known because of the secondary VOCs produced in the calculations vs. what is actually in the atmosphere.

Figure 5 and text. Is the third category of compounds, all those not in category 1 or 2? Compounds whose average is within a factor of two for periods 1 and 2?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 8595, 2011.