**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Ozone production during the field campaign RISFEX 2003 in the Sea of Japan: analysis of sensitivity and behavior basing on an improved indicator" *by* Z. Q. Wang et al.

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1. General comments

The paper investigates the ratio $\Sigma k_{OH}HC/k_{OH}NO_x$ as an indicator for the sensitivity of the ozone production rate ($P(O_3)$) to HC and NO_x. This is one of the most useful of the measurement-based approaches to the problem of evaluating O_3-HC-NO_x sensitivity and deserves to be most widely known. In particular, the ratio $\Sigma k_{OH}HC/k_{OH}NO_x$ appears to be a robust indicator for $P(O_3)$, whereas the simpler ratio $\Sigma HC/NO_x$, which is widely used by regulatory agencies, is only valid for a few specific urban situations. This paper presents useful and interesting results, especially with regard to robustness,

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and includes calculations for widely different situations. I recommend publication.

I believe the paper can be strengthened if the authors show some comparisons with previous results for the ratio $\Sigma k_{OH}HC/k_{OH}NO_x$. These are useful because they would show that the ratio behaves similarly in many diverse situations.

I think that the quality of writing needs to be improved. The paper is difficult to read and will be especially difficult for readers who are not already familiar with the topic. I suggest that the authors revise the paper for clarity. The paper also contains many errors in the use of English language, which make it more difficult to understand. I urge the authors to do careful editing of the final version to improve this.

2. Specific comments

1. It would be very useful to compare the results shown here with Kleinman et al., 2005, Figure 14 (attached). Kleinman et al. did 0-d calculations similar to the calculations in this paper, based on measurements in five cities in the U.S. Their Figure 14 shows $P(O_3)$ versus $\Sigma k_{OH}HC/NO_x$. The maximum $P(O_3)$ (equivalent to Φ_{opt} in this paper) occurs when $\Sigma k_{OH}HC/NO_x=1$ sec^{-1}ppb^{-1} (approximately). This is equivalent to $\Phi_{opt}=4$, and is not inconsistent with the value found in this paper ($\Phi_{opt}=7$ +/-3).

The comparison with Kleinman et al., 2005 is useful because Kleinman et al. also show how $\Sigma k_{OH}HC/NO_x$ compares with their Ln/Q. The Ln/Q is advantageous because it is directly linked to chemistry. More generally, the comparison would help to establish that results are similar for a wide range of conditions.

2. Similarly, it would be useful to give exact comparisons between the Φ_{opt} reported here and the equivalent values from Tonnesen et al. (2000) and Frank et al. (2001). The text states that the results here agree with the conclusion in Tonnesen et al. and Frank et al. (p. 10562, line 23). It would be useful to report the exact values from those papers (and uncertainty ranges) to show how they compare for Φ_{opt}.

3. The description of the four chemical regimes should be presented more clearly. The

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four regimes are first introduced on p. 10555 (line 21), but it is not immediately clear what these regimes are. A clear definition only appears in Section 4.2.

The text should begin with a statement that the authors are identifying four regimes with different $P(O_3)$-NO_x-HC sensitivity. It probably would be useful to define the regimes in terms of $P(O_3)$-NO_x-HC behavior, rather than in terms of detailed chemistry as on p 10555-10556. The definition should be given before the regimes are used in discussion.

4. Also with regard to regimes: The distinction between Regime I versus Regime II and between Regime III and Regime IV are unclear. Are these regimes defined based on the response of $P(O_3)$ to NO_x and HC (as discussed in Section 4.2)? Or are the regimes defined by the relative strength of different chemical reactions, as on p. 10555?

My interpretation is that Regime I is defined by an almost-linear increase in $P(O_3)$ with increasing HC and an almost linear decrease in $P(O_3)$ with increasing NO_x. Regime II is defined by a less-than-linear increase with HC and a less-than-linear decrease with NO_x. Regime III is defined by less-than-linear increases with both HC and NO_x, and Regime IV is defined by a near-linear increase with NO_x and no increase with increasing HC. If this is correct, it may help to state it directly.

5. The description of chemistry (p. 10555-10556) is confusing and contradicts some previous analyses.

Here, the text refers to competition between OH+HC and OH+NO2 (p. 10555, line 22, p. 10556, line 8) as a major factor in determining the behavior of the system. If this competition is important it would provide a direct rationale for the ratio Phi as an indicator for sensitivity to NO_x and HC. However it is not clear whether this competition has a direct impact on sensitivity.

By contrast: Kleinman et al., 1997 and Sillman, 1995, the most important feature of chemistry is the indirect competition between OH+NO2 and HO2+HO2/RO2 as sinks

for odd hydrogen radicals. There is also influence OH+HC and HO2+NO, which largely determine the HO2/OH ratio. These results were based on mathematical derivations for a simplified system, and may be more valid as an explanation.

6. Also on chemistry: results from Sillman (1995) may be useful in explaining the behavior found here. Sillman found that the transition from NO_x-sensitive to HC-sensitive conditions is in theory linked to $\Sigma k_{OH} HC/NO_x$. Specifically, the transition should occur when

$\Sigma k_{OH} HC/NO_x = k\ P(O_3)/(S_H - P_{PAN})$

where S_H is the radical source (=Q in Kleinman et al., 2007).

This was a result 'in theory' based on simplified chemistry. Here, results (p. 10564, line 5, and Figures 7-8) based on detailed calculations show that Φ_{opt} decreases when factors related to S_H are increased. The simplified solution from Sillman (1995) may provide an explanation. As above, this explanation is driven by the competition between sinks for odd hydrogen radicals (as in Ln/Q) and the HO2/OH ratio.

7. Some additional details are needed in the model description (Section 3).

How is the sensitivity of $P(O_3)$ to NO_x and HC (Figures 4 and 5) calculated? Is this based on repeat calculations of $P(O_3)$ with a small change in NO_x or HC? The text (p. 10561, line 11) only says that sensitivity was calculated. Please state exactly how the calculation is done.

The text (p. 10562, line 8) refers to calculations for $d\ \ln P(O_3)/\ d\ \ln[NO]$ and $d\ \ln P(O_3)/\ d\ \ln[HC]$ based on Equations (1) and (2). This is unusual because Equations (1) and (2) represent an attempt to estimate $d\ \ln P(O_3)/\ d\ \ln[NO]$ and $d\ \ln P(O_3)/\ d\ \ln[HC]$ based on parameters (Ln and Q) that might be estimated from measurements. In a model calculation it is appropriate to calculate these by repeating the calculation with a small change in NO_x or HC. It is true that Kleinman's formula (Equations 1 and 2) appear to work very well as an approximation to model values, but it is somewhat unusual to use

this when model results are available.

How are the concentrations of unmeasured 'intermediate' organics set (MGLY, MACR, PAN)? Are these initially set at 0 and allowed to increase with time? Do they change in calculations with changed NO_x and HC for the sensitivity calculations?

8. The results in secton 4.4 (Figure 10) comparing measured versus model $P(O_3)$): It would be useful to briefly refer to the many similar studies that have evaluated model vs. measured $P(O_3)$ or HO2, for example: Ren et al., 2008, Shirley et al., 2006, Thornton et al. (2002).

Also, on p. 10566, line 12: "The model tends to underestimate $P(O_3)$ when $P(O_3)$ is greatly sensitive to HC. It indicates an important source of RO2 radicals from BVOC". Why does this need to be BVOC? The underestimate could be due to biogenic VOC (consistent with Qi et al., 2007) but it could also be due to underestimated RO2 from anthropogenic VOC, or from unmeasured VOC.

3. Technical corrections

p. 10553, line 24: "The relative sensitivity of $P(O_3)$ to NO and HC, *d* ln$P(O_3)$/ d ln[NO] versus *d* ln$P(O_3)$/ dln[HC], which are defined as... ". "defined" is incorrect. Equations (1) and (2) are derived from chemistry. It should be:

"The relative sensitivity of $P(O_3)$ to NO and HC, *d* ln$P(O_3)$/ d ln[NO] versus *d* ln$P(O_3)$/ dln[HC], were found to be equal to... "

p. 10555, line 17: Monte Caro -> Monte Carlo

p. 10557, line 26: Furth more -> Furthermore

p. 10560, line 29: rang -> range p. 10562 line 23: during our observation

p. 10566, line 13: photochemistry -> photolysis. (Photochemistry refers to all chemistry under the influence of light, not just the photolysis reactions.)

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p. 10563: frequent use of abbreviations for chemical species (ISO, ALD, TOL, MACR). The species names should be stated explicitly.

p. 10563, line 26: "MACR from the sea". Methacrolein (MACR) is usually produced from the reaction of isoprene with OH and subsequent reactions.

p. 10565, line 9: "Form" -> From.

Reference to Ren et al., 1987 is incorrect. The reference should be Trainer et al.

Figure 9 caption: What are the green and blue lines? The caption should say.

Language issues: There are errors in English usage and grammar throughout the paper. Some examples: p. 10556, line 10, p. 10567, line 26; p. 10570, line 12, and the title ("basing" should be "based").

4. References

Kleinman, L. I., P. H. Daum, Y.-N. Lee, L. J. Nunnermacker, S. R. Springston, J. Weinstein-Lloyd, and J. Rudolph (2005), A comparative study of ozone production in five U.S. metropolitan areas, J. Geophys. Res., 110, D02301, doi:10.1029/2004JD005096.

Ren , X., et al. (2008), HOx chemistry during INTEXâĂŘA 2004: Observation, model calculation, and comparison with previous studies, J. Geophys. Res., 113, D05310, doi:10.1029/2007JD009166.

Shirley, T. R., Brune, W. H., Ren, X., Mao, J., Lesher, R., Cardenas, B., Volkamer, R., Molina, L. T., Molina, M. J., Lamb, B., Velasco, E., Jobson, T., and Alexander, M.: Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003, Atmos. Chem. Phys., 6, 2753-2765, 2006.

Sillman, S. The use of NOy, H2O2 and HNO3 as indicators for ozone-NOx-ROG sensitivity in urban locations. J. Geophys. Res.,100, 14175-14188, 1995.

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Thornton, J. A., et al. (2002), Ozone production rates as a function of NOx abundances and HOx production rates in the Nashville urban plume, J. Geophys. Res., 107(D12), 4146, doi:10.1029/2001JD000932.
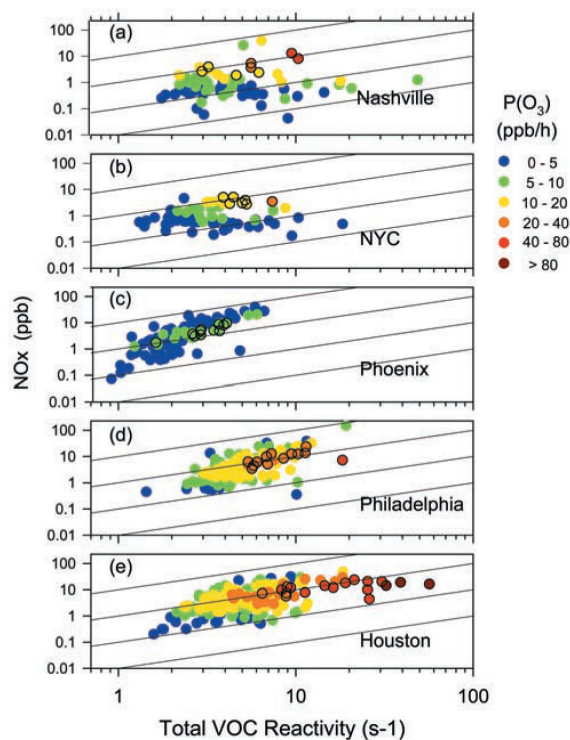
Fig. 1. Ozone production rates for five cities displayed as color-coded symbols as a function of VOC reactivity (sec$_{-1}$) and NO$_x$ concentration (ppb). From Kleinman et al., 2005 (Figure 14).