**Atmospheric
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Discussions**

Interactive comment on "A scaling analysis of ozone photochemistry: II Investigation of the similarity relationship" *by* B. Ainslie and D. G. Steyn
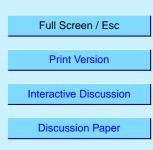
B. Ainslie and D. G. Steyn

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We thank the reviewer for their comments. Here, we respond to the issues raised in the review, and additionally, we have modified the original papers to reflect these disc

Comment I
Figure 1 and 3 give $P(O_3)$'s that follow from specified Properties. What I really want to see are the $P(O_3)$'s that follow from the third model that incorporates the need for a change in functional form to produce a scaling break. A change in functional form is not a stand-alone concept without an example.

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We have included a new figure schematically showing $P(O_3)$ curves for two mixtures having a common NOx concentration but different VOC concentrations. This should serve to illustrate the change in functional form.

Comment II

There are 2 other major items missing: 1). A sense of how $P(O_3)$ integrated over time yields points on an isopleth diagram. I think that would require explicit $P(O_3)$ diagrams. There has been modeling and field work directed at examining $P(O_3)$ in the limiting cases of high NOx and high VOC environments, so I would expect, the $P(O_3)$'s to match up with those limiting cases. I hope at the least that this will be in Part III.

Reply

To develop the link between $P(O_3)$ and maximum ozone concentrations on an isopleth diagram, it is easiest to start with the isopleth diagram and imagine a horizontal line running across the diagram at a constant value of NOx ($[NOx]_o$). Plotting the corresponding ozone concentrations along this line as a function of initial VOC concentrations essentially gives the similarity relationship. To actually reproduce the similarity relationship, first one must normalize all ozone concentrations by the maximum value found along this line (which is simply $\gamma[NOx]_o^a$). Next, in order to over-plot ozone concentrations taken along all other constant NOx lines, one must internally scale the VOC axis by the NOx concentration along each line (i.e. plot $[VOC]_o/[NOx]_o$). When this is done, an ozone isopleth surface is collapsed onto a 2D curve. Finally, the link between the similarity function and $P(O_3)$ curves is outlined in II Section 2. This description is outlined in the first footnote in the second paper. We have expanded this section and placed in the main text.

Comment III

Secondly, a discussion of what chemical features in the mechanism cause the scaling break. Is there any way to relate the scaling break to compounds that one measures? There is a speculation that 'the change can be understood in terms of the strength of NOx inhibition occurring with in a VOC-NOx mixture'. That and the following discussion

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are not very illuminating.

Reply

The scaling break does not appear to be related to any single parameter in any of the mechanisms we have studied. In fact, we have found it sensitive to changes in many rate constants and reaction products. In addition, changes which affect β often affect the other parameters. We have explored various methods and ideas for the interpretation of the scaling break (Ainslie,2004) and from these analyses, we find it more insightful to focus on what occurs across the scaling break than to focus on the break itself. Recall from Eq.(9) of the first paper (Ainslie and Steyn, 2005) that it is the shape parameter (α) that changes across the break. For the RADM2 mechanism, we find α_1 shows more variability between VOC classes than does α_2 (which is largely independent of VOC class). In a simple autocatalytic description of ozone formation, ozone production is initially slow because it is limited by radical availability. But as ozone concentrations begin to rise, ozone acts as a radical source, increasing its own production rate. This positive feedback leads to conditions with elevated NO_2 and $OH^\bullet$ concentration which spurs on HNO_3 formation, limiting ozone production. From another point of view, when additional NO_x is added to a VOC-NOx mixture, ozone concentrations decrease because: initially, there is more NO that has to be oxidized to NO_2; this greater amount of NO to oxidize causes ozone formation to occur later, delaying the inorganic production of radicals; and finally, increased NO_2 concentrations favour the production of HNO_3. As a result, VOCs that can produce their own photolytic radical source can alleviate this dependence of ozone production on ozone concentration – that is, they should show less NOx-inhabition.

From the perspective of the scaling model, we find $HCHO$, which readily produces radicals through photolysis, has the lowest α_1 value (1.5) while $TOLU$, with the highest value (3.1), does not photolyze nor does it produce many carbonyl compounds as OH-reaction products. Furthermore, it is possible to show α_1 is directly associated with the tilting of ozone isopleths above the ridgeline (Ainslie,2004), which can be viewed

as a geometric representation of NOx-inhibition. On the other side of the break, ozone formation appears to be less dependent on VOC species, which might be expected under NOx-sensitive conditions. We also find the scaling break to be closely associated with a fixed value of the fraction of $HO_2^\bullet$ radicals that react with NO (f_{HO2+NO}) (Ainslie,2004). It is less closely associated with a maximum in OH-chain length that occurs above the ridgeline and also with the peak in $OH^\bullet$ production also seen above the ridgeline (Jeffries, 1995). We have included these remarks in a discussion section in second paper.

Comment IV
Regarding notation: Part I deals with maximum O_3 and Part II mainly with the time dependent O_3. An unambiguous notation to denote time dependent quantities would help.

Reply
To make the notation less ambiguous, we have used the subscript 'max' with all ozone concentrations that refer to maximum ozone concentrations and the subscript '(t)' for time dependent ozone concentrations.

Comment V
Definition of $P_j(O3)$ as the sensitivity of ozone concentrations to the integrated NO_2 photolysis rate constant. Maybe its obvious, but it cant hurt adding that at constant j, $P_j(O3)$ is the ordinary O_3 production rate. This is a very meaningful quantity to the community as it is routinely calculated from precursor observations or from measured peroxy radicals and NO.

Reply
We have included below Eq.(3) that if the actinic flux is fixed so that j_{NO2} is constant then $j(t)$ is proportional to t and $P(O_3)$ is proportional to $P_j(O3)$.

Comment VI
'Most precursor mixtures are initially radical limited'. True for urban mixtures, but not

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true in general.

Reply
We agree that urban mixtures tend to have a greater relative abundance of NO_x to VOC (low R-values) and hence tend to be radical limited. We also find the chemical mechanisms show there is a noticeable lag between the start of the irradiation and the onset of accelerated ozone production for mixtures with high R-values. This suggests mixtures with large VOC to NO_x ratios still show some initial radical limitation. However, in the text, we have changed the phrase to read 'most urban precursor mixtures ...'.

Comment VII
Typo - should be dependence of $P_j(O3)$ on $[VOC]_0$ and $j(t)$.

Reply
We have corrected this error in the text.

Comment VIII
Where did the c=1.2 and beta = 9.4 come from?

Reply
These values came from a regression against model output similar to the 'universal' regression for OLT performed in I Sec 4 . We have changed the text make this clear.

Comment IX
The 's-shaped' profile, does not look very s-shaped.

Reply
The reason the similarity curve in I Fig 1 does not appear to 's-shaped' is because the horizontal axis has been compressed in order to show the curve approaching its limiting value at large R-values. We have now made explicit mention of this in the first paper.

Comment X

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Equation (4), it is not apparent to me where the $P(O_3)$ functional form changes in this equation. Do I have to differentiate with respect to time?

Reply

The shape parameter ($\alpha(R)$) in Eq. (4) changes across the scaling break and we clarify this in the text.

Comment

Would scaled O_3/scaled $NOx^{0.6}$ curves lie on top of each other for the 3 NOx values?

Reply

Plotting dimensionless ozone divided by dimensionless NO_x^a would in fact collapse all 9 curves in Figure 4 onto a single curve (when plotted as a function of Rj^c). We did not do this because it is difficult to distinguish the symbols representing the different simulations when the curves lie ontop of one another. We have included this point in the text.

References

Ainslie, B. and Steyn, D. G.: A Scaling Analysis of Ozone Photochemistry: I Model Development, Atmospheric Chemistry and Physics Discussions, (this issue), 2005.

Ainslie, B. D.: A Photochemical Model Based on a Scaling Analysis of Ozone Photochemistry, Ph.D. thesis, University of British Columbia, Vancouver, B.C., Canada, 311 pp., 2004.

Jeffries, H. E.: Composition, Chemistry & Climate, chap. 9. Photochemical Air Pollution, pp. 308–348, Van Nostand-Reinhold, 1995.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 12985, 2005.

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