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Interactive comment on "A scaling analysis of ozone photochemistry: I Model development" *by* B. Ainslie and D. G. Steyn

B. Ainslie and D. G. Steyn

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Interactive Comments on 'A Scaling Analysis of Ozone Photochemistry: I Model Development' by B. Ainslie and D. G. Steyn

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

Referee 1

Comment I

A table of non-dimensional quantities would make the text much easier to follow.

Reply
We have included a table of non-dimensional quantities with their definitions in the paper.

Comment II
'Third, we try a power law for the π_2/π_5 dependence.' It is not clear until you see Eq.(5), that this sentence refers to the dependence of π/π_5 on π_2/π_5.

Reply
We have make the reference to π/π_5 explicit in the sentence.

Comment III
It would be helpful to also spell out the equations using symbols that bring to mind the physical quantities.

Reply
We have included a version of Eq.(5) written in symbols which are more easily understood in terms of their physical quantities.

Comment IV
It would be helpful to add $= f(R)$ after equation 6.

Reply
We have made this revision in the text.

Comment V
The term 'Weibull transformed' is an idiosyncratic phrase.

Reply
We have reworded this line to read: 'To test the suitability of the Weibull function, the dimensionless model output was normalized and transformed using the inverse Weibull

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function:

$$W(f(R)) = \ln\left(\ln\left(\frac{1}{1-f(R)/\gamma}\right)\right) \quad (1)$$

If the Weibull function fits the similarity relationship, then the transformed model output should cluster along a straight line when plotted as a function of $\ln R$.'

Comment VI

Is there a way of picturing the shape parameter using the functional form of a lognormal.

Reply

The shape parameter (α) takes on two values (α_1 and α_2) depending on the magnitude of R. We choose to describe this behaviour using a $tanh$ function to make the similarity function smoother. This parameterization does not add anything to the development of the ideas, and to simplify the model, we now define the shape parameter as follows:

$$\alpha(R) = \begin{cases} \alpha_1, & R < \beta \\ \alpha_2, & R \geq \beta \end{cases} \quad (2)$$

Comment VII

If $P(O_3)$ is proportional to NO_x for the whole time evolution why isn't $[O_3]_{max}$ proportional to NO_x?

Reply

At large R, $[O_3]_{max}$ is proportional to the *initial* NO_x concentration raised to the 0.6 power ($[NO_x]_o^{0.6}$). We have not analyzed the relationship between maximum ozone concentrations and the time integrated (or average) NO_x concentration.

Comment VIII

Should $ln(R/b)$ be $ln(R/\beta)$?

Reply

This is correct and we have changed this typographic error.

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Comment IX
For the OLT chemistry, how many parameters are needed without the light and temperature dependence?

Reply
Six parameters are needed to parameterize the OLT chemistry: one to normalize the scaled model output (γ), one for the NO_x scaling exponent (a), two for the location of the scaling break (β,λ) and two for the slopes of the line segments (α_1,α_2) (in the Weibull plane). We now explicitly state this in the paper.

Comment X
Does the task of representing different VOCs become easier if a VOC reactivity axis is used in Figure 3?

Reply
The idea of using a reactivity axis to simplify results is interesting since VOC 'reactivity' can be viewed as a type of scaling i.e. within a limited range of conditions, it is assumed there is a measure of ozone formation that allows the behaviour of the photochemical system to be considered independent of VOC. Unfortunately, there are different criteria for measuring 'reactivity' and typically with these definitions, the 'reactivity' of a specific species is highly dependent on whether or not other VOCs are present – making it is impossible to develop an absolute measure of VOC reactivity. For a single VOC species, the sensitivity of maximum ozone concentrations to changes in its initial concentration is called the incremental reactivity (IR) (Carter,1994) and is often used as a measure of reactivity. Using the scaling model with constant environmental conditions this can be functionally described by:

$$IR = \frac{\partial [O_3]_{max}}{\partial [VOC]_o} = \gamma \left(j_{av}/k_{NO}\right) \left(\frac{[NOx]_o}{j_{av}/k_{NO}}\right)^a f'(R) \frac{dR}{d[VOC]_o} \quad (3)$$

This reactivity scale has a NO_x dependence which can be removed by creating a

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'NOx-scaled' incremental reactivity (NSIR):

$$NSIR = \frac{IR}{\left(\frac{[NOx]_o}{j_{av}/k_{NO}}\right)^{a-1}} = \gamma f'(R) \quad (4)$$

which is now a function of R only. However, this NOx-scaled reactivity shows VOCs should only be compared when the relative abundance of VOC to NO_x (R) is considered; consistent with observations by Carter and Atkinson (1989) who suggest the VOC/NO_x ratio is the most important factor affecting reactivity. To produce a single valued VOC reactivity, one can decide to evaluate the NSIR at a specific R-value. Choosing this R-value to produce the NSIR with the maximum value means evaluating it at:

$$R_{MIR} = \beta \left[\frac{\alpha_1 - 1}{\alpha_1 \lambda}\right]^{1/\alpha_1} \quad (5)$$

We have done this and find reactivities calculated in this manner correlate well with other reactivity scales. This matter is dealt with in detail in Ainslie (2004) but we judge the matter to be beyond the scope of this paper.

A less sophisticated way to account for VOC reactivity is by scaling VOC concentrations by β and plotting ozone isopleths using $[NOx]_o$ versus $[VOC]_o/\beta$. This method also has the nice feature that both axes of the isopleth diagram are now in terms of NO_x concentrations (since $\beta = [VOC]/[NOx]$) and if both axes have the same scale, then the isopleths are free from distortion. Of course, the 'universal' similarity plot (Figure 5) is essentially presented this manner and gives the same information as set of isopleths over-plotted on a single set of axes.

When VOCs of greatly varying reactivities are to be compared, plotting ozone isopleth using $[NOx]_o$ and $[VOC]_o/\beta$ is not sufficient to collapse the model output onto a single set of isopleths. This can be seen by looking at the wide range of slopes for the Weibull transformed similarity relationships in Figure 4. The only instance where plots of maximum ozone concentration as a function of $[NOx]_o$ versus $[VOC]_o\beta$ produce a single

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set of isopleths for different VOCs is with model output from the highly parameterized Generic Reaction Set (GRS) (Azzi,1992) mechanism. In this case, ozone isopleths for the mechanism's reactive organic compounds (ROCs) having different reaction rates, are identical when initial ROC concentrations are scaled by β. Again, we feel the inclusion of these ideas into the current paper would make it too lengthy.

Comment XI

Is the curve in Figure 1 the prototypical S shaped relation? If so, you should explicitly call attention to the small hook on the bottom which does not visually stand out.

Reply

Yes, Figure 1 is typical of many of the similarity relationships and we have included a sentence to highlight the small hook occurring for small R-values. The 'shaped' nature is not as noticeable in this figure because we have scaled the horizontal axis in order to accommodate a large range of R-values.

References

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.

Azzi, M., Johnson, G. M., and Cope, M.: An introduction to the Generic Reaction Set, in: Proceedings of the 11th international Clean Air Conference, Brisbane Australia, 1992.

Carter, W. P. L.: Development of Ozone Reactivity Scales for Volatile Organic Compounds, Journal of the Air and Waste Management Association, 44, 881–899, 1994.

Carter, W. P. L. and Atkinson, R.: Computer Modeling study of Incremental Hydrocarbon Reactivity, Environmental Science and Technology, 23, 864–880, 1989.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 12957, 2005.