**Atmospheric
Chemistry
and Physics
Discussions**

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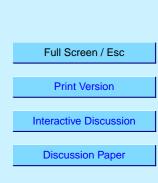
B. Ainslie and D. G. Steyn

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Note: Since this reviewer submitted a single review for both *A Scaling Analysis of Ozone Photochemistry: I Model Development by B. Ainslie and D. G. Steyn* and *A Scaling Analysis of Ozone Photochemistry: II Investigation of the similarity relationship by B. Ainslie and D. G. Steyn*, we have submitted a single set of Author's Comments for both papers.

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

Comment I

Full Screen / Esc

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I have difficulties to see the relevance of the results. From the numerical point of view Eq.(11) or related equations are of no advantage with respect to box model calculations.

Reply

As motivated in Section 1 (Introduction) of the first paper, the goal of this paper is to describe the gross behaviour of a photochemical mechanism in terms of a small set of variables. From this perspective, the work is not unlike that of Johnson (1984), Chang and Rudy (1993), Chang et al. (1997), Wang et al. (2001) and Shenvi et al. (2004) except our approach is through formal dimensional analysis which is central to this paper. While we do end up fitting a curve to our similarity function, the conceptual basis of the first paper is to capture integrated response of a complex system in terms of a small set of non-dimensional groups. The goal of the second paper is to interpret the similarity relationship, introduced in the first paper. We argue that the papers have:

- Provided a new application of dimensional analysis and scaling to study the integrated behaviour of a photochemical mechanism.

- From the dimensional analysis, we have developed a similarity relationship which characterizes the sensitivity of maximum ozone concentration to initial precursor concentrations. This similarity relationship shows a scaling break.

- Developed a parameterization of the similarity relationship, using a composite Weibull function, which provides a much better model for ozone-precursor relationships than Chang and Rudy (1993); and is valid in the NO_x limited region, around the ridgeline and in parts of the VOC limited region.

- Developped a parameterization which includes the influence of temperature and actinic flux on the integrated model behaviour.

- Shown that the qualitative features of the similarity relationship and scaling anal-

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ysis hold for a wide range of VOCs, VOC mixtures, and for other chemical mechanisms.

- Have developed a semi-qualitative model for ozone production which generalizes the IER model and is consistent with the similarity function.

- Used the scaling analysis and dimensionless groups to develop a novel way of presenting smog chamber data.

Comment II
From a more fundamental point of view the scaling approach could be a potentially interesting, but that has not been discuss in the paper. To name a few of the questions I have in mind:

1. Is the approximate validity related to the fact the chemistry consists of first and second order reactions only?

2. To what extend are the scaling properties caused the close relation between $J(NO2)$ and $J(O3->O(1D))$ [limiting rate for OH-production], since degradation of VOCs by $OH^\bullet$ is in turn the rate limiting step for ozone production.

3. Is the fact that the scaling is successful merely a consequence of the numerical flexibility of the fit expression with 8 parameters?

4. What is the reason for lack of success for the slow reacting HCs?

5. Can the relation be used to analyze measured data?

Reply

1. Obviously if all of the reactions were zeroth order, no scaling would arise as ozone concentrations would not be dependent on the abundance of other species. The presence of more third order reactions (there are a few already in the RADM2 mechanism), would not likely prevent scaling relationships from holding. The presence of these more complex reactions might lead ozone concentrations to be influenced by a larger number of other species. The integrated effects of these new dependencies should in principle be amenable to a scaling level analysis (of course this may lead to different dimensionless groups and different dependencies).

2. Ozone formation can be viewed in terms of competing processes, of which radical formation (which is strongly influenced by ozone photolysis) and radical propagation (which is dependent on OH-attack on VOCs) are two important examples. As we mention in the discussion following the development of the 'universal' similarity function (Section 4), the scaling is successful because of the ability to identify dimensionless groups associated with the various principal chemical processes.

3. As mentioned above, the scaling is successful because of the ability to identify dimensionless groups associated with the key chemical processes. Evidence of the success of the scaling analysis is given by the similarity relationships seen in Figures 1 and 5. The fitting of a curve to these relationships is merely a means of quantifying the similarity relationship and should not be confused with the scaling itself. We have added this point in the in Paper I section 4.2.

4. As we mention in the text, we believe the slow reacting HCs do not show any scaling because with these compounds, the photochemical system lacks radical sources (other than ozone itself) and have increased NO_x and peroxy radical losses arising from organic nitrate formation. These important chemical pathways for NO_x were not considered when developing the scaling parameters. Capturing the direct influence of these new pathways likely requires the inclusion of addition

key variables and the formation of different dimensionless groups.

5. As we show in the second paper (section 5), this scaling framework has allowed us to present observations from smog chamber tests, conducted under a variety of conditions, on a single graph. In the conclusion section in the second paper, we suggest this framework could be used to analyze ambient ozone concentrations drawn from a variety of environmental conditions.

Recommendations

Recommendation I
The paper should focus on the discussion of the existence of the universal relationship and its possible chemical reasons.

Reply
The universal similarity relationship arises because the integrated behaviour of the VOC to NO_x ratio, temperature and the level of actinic flux on maximum ozone concentration can be captured by a power law relationship involving a small number non-dimensional quantities. None of the scaling parameters appears to be directly related to any rate constants or reaction products in the chemical mechanisms studied. Instead, the scaling parameters appear to be related to sub-processes within the photochemical system. For instance, the dependence of the similarity relationship on R suggests that once maximum ozone concentrations have been normalized by initial NO_x concentrations (which itself is proportional to the highest ozone concentrations that can be achieved for a given initial NO_x concentration; independent of VOC concentration (Blanchard et al.,1999), the photochemical system's behaviour with respect to this scaled ozone concentration depends only on the relative abundance of VOC to NO_x. From a radical propagation perspective (Tonnesen and Dennis,2000), R acts as a surrogate for the sensitivity of ozone production to an increase in the fraction of $OH^{\bullet}$ radicals reacting with VOC at high VOC concentrations and to an increase in the frac-

tion of $HO_2^\bullet$ radicals that react with NO at high NO_x concentrations. The dependence of the scaling break (β) on actinic flux (J) suggests increasing J causes the switch in regimes to occur for lower R-values but otherwise leaves the integrated behaviour of the photochemical system unchanged. The power law dependence on T suggests the integrated effects of temperature on ozone affects only the magnitude of the final concentrations while leaving the R and J dependencies unchanged (this is an approximation, since temperature also affects the scaling break with increasing temperatures causing the break to occur at smaller R-values (Ainslie,2004). We have include more detail about the relationship between scaling parameters and the underlying chemistry in the discussion of the 'universal' similarity relationship.

Recommendation II
As mentioned above the scaling approach is no useful tool if numerical values are desired. The straight forward way to compute maximum ozone is to invoke a numerical model calculation solving the balance equations. There is no need for simplifications like Eq.(11). Therefore numerical aspects related to the calculation maximum ozone should be substantially shortened and limited to strengthen arguments under first recommendation.

Reply
We agree that running a box model with a chemical mechanism is fast and a more accurate way to calculate ozone concentrations. However equations 9 or 11 can be used to estimate ozone concentrations within a bigger integrated assessment model where computation resources are limited. We have added this point to the conclusions. Furthermore, we think it is important in paper I to provide an in-depth discussion about the selection of key variables; how these relate with other research; and the numerical modeling set-up. We introduce the Weibull transform in order to show the scale break. We also provide detailed description of the methods used in the 'universal' scaling.

C. Recommendation
The manuscript should be combined with the paper II. It continues the discussion on

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a scale break which has already been addressed in paper I and is associated with a change of the temporal development of the ozone mixing ratio.

Reply

We have carefully considered this idea but given the technical nature of the paper and its new methods and ideas, it would be difficult to combine the two papers without without making it too cryptic and dense.

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