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Discussions

Interactive comment on "A new diagnostic for tropospheric ozone production" *by* Peter M. Edwards and Mathew J. Evans

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Anonymous Referee #1 This paper presents a novel analysis of ozone production in terms on the spin states of the bonds in the precursor species. This is an interesting and original concept, and is a commendable attempt to generate a diagnostic of ozone production that has a sound physico-chemical basis, and one that provides more process insight than the standard methods based on NOx cycling. The paper is worthy of publication, but needs revision to address a number of weaknesses and to enhance its value to the scientific community.

General Comments

1) The background theory behind the diagnostic could be presented more clearly.

While the concept of electron spin is well understood in the physical chemistry community, it is necessary to provide a brief introduction for a wider audience, along with references to literature where readers can learn more.

Response: The paragraph in the introduction that introduces spin has been expanded and a reference to an explanation of the fundamental principles included. This paragraph now reads:

Change to manuscript: The inefficiency of ground state O2 as an atmospheric oxidant is due to its electronic structure. In quantum mechanics, all atomic particles have an intrinsic angular momentum known as spin [Atkins and De Paula, 2014]. The spin of an electron is described by the spin quantum number, s, and can have values of either $+\frac{1}{2}$ or $-\frac{1}{2}$ for a single electron. The Pauli exclusion principle states that if two electrons occupy the same orbital then their spins must be paired, and thus cancel. With two unpaired electrons ground state O2 is a spin-triplet with a total spin quantum number $S=\frac{1}{2}+\frac{1}{2}=1$ (giving a term symbol of (_ˆ3)Σ_gˆ-). In contrast, virtually all trace chemicals emitted into the atmosphere contain only paired electrons and are thus spin-singlets (S=0). The quantum mechanical spin selection rule $\Delta S=0$ means that allowed electronic transitions must not result in a change in electron spin. From a simplistic perspective (i.e. ignoring nuclear spin interactions, inter-system crossings, nuclear dipole effects etc.) this spin selection rule means that the reaction of ground state O2 with most emitted compounds is effectively spin forbidden. Electronically excited O2 ((_ˆ1)Δ_gˆ or (_ˆ1)Σ_gˆ+) is a spin singlet and is more reactive in the atmosphere but low concentrations limit its role [Larson and Marley, 1999]. Instead, atmospheric oxidation proceeds predominantly via reactions with spin-doublet oxygen-derived species ($S=\frac{1}{2}$), notably the hydroxyl (OH) and peroxy radicals (RO2 = HO2, CH3O2, C2H5O2, etc.), or spin-singlet species (e.g. ozone (O3)).

2) The paper addresses the rate of ozone production, but discussion focuses solely on long-term integrated ozone production on an annual global scale. It is not clear how applicable the new diagnostic is to smaller regions and shorter timescales where the

assumption of steady state (line 141) may be less appropriate, and where emissions may be less important than transport. What is needed to extend the diagnostic to these smaller spatial and temporal scales? The potential for analysis of regional budgets is alluded to on line 307, but no detail is provided.

The strengths and limitations of the approach should be set out more clearly. What additional insight does the new metric provide and how might this be applied to real problems (e.g., to the sensitivity of ozone production to assumptions of VOC speciation, to simplification of isoprene chemistry, or to treatments of deposition processes?) How does the approach compare with previous attempts to generate diagnostics, e.g., though the concept of photochemical ozone creation potentials (POCPs) for individual VOCs? There is little reference to earlier approaches in the field.

Response: The aim of this paper is to describe a new approach for the study of ozone production in chemical transport models, and to illustrate this through a global budget analysis and comparison with the most commonly used diagnostic for this. The application of the new diagnostic to other scales and problems, as well as comparison to other available metrics is of interest but unfortunately outside the scope of this work. The following paragraph has been added to the conclusion section to discuss the strengths of the approach in relation to other possible applications, and also identify things that would need to be considered for this to be successful.

Change to manuscript: Future work is necessary to identify the usefulness of this approach on smaller spatial and temporal scales. For regional modelling scale, the transport flux of bonds into the domain would need to be considered alongside the emissions of bonds. However, this might help to disentangle O3 production due to local VOC emissions from that due to VOC emissions outside of the domain. This bond focussed approach may also have usefulness on shorter timescales. For example, when considering vertical fluxes in and out of the boundary layer, a bond centred approach could help. What fraction of the bonds emitted at the surface are exported to the free troposphere. If a measurement of reactivity flux could be made this could be

tested experimentally.

Specific Comments

3) Figure 4: please explain how the contributions of the R and F terms presented in the figure are derived. It is easy to see for the standard diagnostic, where the terms sum linearly to the total PO3, but it is not as clear for the new diagnostic as the terms are no longer independent of each other (as defined in Eq. 1).

Response: The following text has been added to the figure caption.

Change to manuscript: The PsO3 diagnostic parameters are derived for each model simulation using the diagnostic implementation described in Sect. 3, and the fractional change in each parameter from the base simulation calculated.

4) The meaning of the horizontal dashed lines in Figure 4 is not clear.

Response: These are gridlines to aid comparison between plots. We have not changed this as we feel it helps interpretation of the figure, but are happy to take the editors guidance.

5) l.270: How many simulations were performed for these sensitivity studies? Please state this in the text.

Response: Text now includes following sentence.

Change to manuscript: A set of 5 simulations was performed for each model sensitivity investigated (NOx, isoprene and CH4), with a common base simulation, resulting in 13 simulations in total.

6) Figure 7 is not well conceived. It is not clear why a log-NOx scale is used, given that the relationships expected are not exponential (neither line drawn here is expected to be straight, as would quickly become evident at larger or smaller NOx levels). Perhaps plot OH vs CH4 bond emission directly, and label the points with the NOx level?

Response: We thank the reviewer for this suggestion and have updated the figure to that attached (attached Fig1).

Change to manuscript: Updated figure with new caption "Figure 7. Effective CH4 emissions as a function of global mean OH concentration, for simulations where NOx emissions were changed. Marker size and colour indicate global NOx concentration.".

7) Figures 8 and 10 would be more effectively presented through the use of a bar chart, so that the relative changes can be seen more clearly.

Response: We again thank the reviewer for this suggestion and have remade the figures as bar charts (see attached Figs 2 & 3).

Change to manuscript: Updated figures with new captions "Figure 8. Oxidisable bond loss mechanism fractions under changing effective CH4 emissions (0.5 x CH4 concentration field, base simulation and 2 x CH4 concentration field)." and "Figure 10. Oxidisable bond loss mechanism fractions under changing isoprene emissions.".

8) Supplement: The "errors in chemistry scheme" need some explanation, and these entries should be at the bottom of the table, as it doesn't aid the reader's comprehension to put them at the top.

Response: We have added the following text to the supplement and moved the entries to the bottom of table S1.

Change to manuscript: Inconsistencies within the chemistry scheme, where the lumped nature of some reactions result in a non-physical production or loss of oxidisable bonds, are also tracked as errors in the chemistry scheme.

9) The supplement needs more detail on the implementation of the approach. It would be difficult for anyone to replicate in a different model without more information about the reaction classification. It would be helpful to provide a worked example of how the multiple in the Table is arrived at, and this could be included in the supplement.

Response: The following has been added to the supplement.

Change to manuscript: Reaction tags were added to all reactions in the chemistry scheme, and the GEOS-Chem diagnostic was used to provide a direct measure of their production. An example of how this was implemented is shown below for a select few steps of the methane oxidation scheme illustrated in Fig. 1. CH4 + OH → CH3O2 + 1[Tag1] + 1[Tag2] + 1[Tag3] CH3O2 + HO2 → CH3OOH + 1[Tag4] + 1[Tag5] CH3O2 + CH3O2 → CH3OH + CH2O + 2[Tag6] + 1[Tag7] Reaction tags used in example reactions: Tag1 = Oxidisable bond lost via OH chemical reaction; Tag2 = Oxidisable bond + OH → 1 radical (RO2); Tag3 = OH + CH4 reaction (special tag used to calculate effective CH4 emission); Tag4 = RO2 to peroxide; Tag5 = HO2 to peroxide; Tag6 = RO2 lost to carbonyl forming peroxy radical self reaction; Tag7 = Bond lost to RO2 + RO2 → 0 radicals. Typos and minor issues

10) The English grammar needs a little work in places, particularly where the subject of a verb is inappropriate (e.g., "GEOS-Chem fixes CH4 concentrations..." on line 318 would be clearer as "CH4 concentrations are fixed in GEOS-Chem...")

Response: This has been addressed.

11) l.133: add the before top

Response: This has been addressed.

12) l.251: grammar in first sentence needs correcting.

Response: This has been addressed.

13) l.358: MO2 should be written as CH3O2 for consistency with line 356, and it would be helpful to do this throughout the text, e.g., line 427/8.

Response: This has been addressed.

14) Numbers less than 10 without units are better presented as text than numerals.

Response: This stylistic change has not been implemented, but the authors are happy to do so if the editor wishes.

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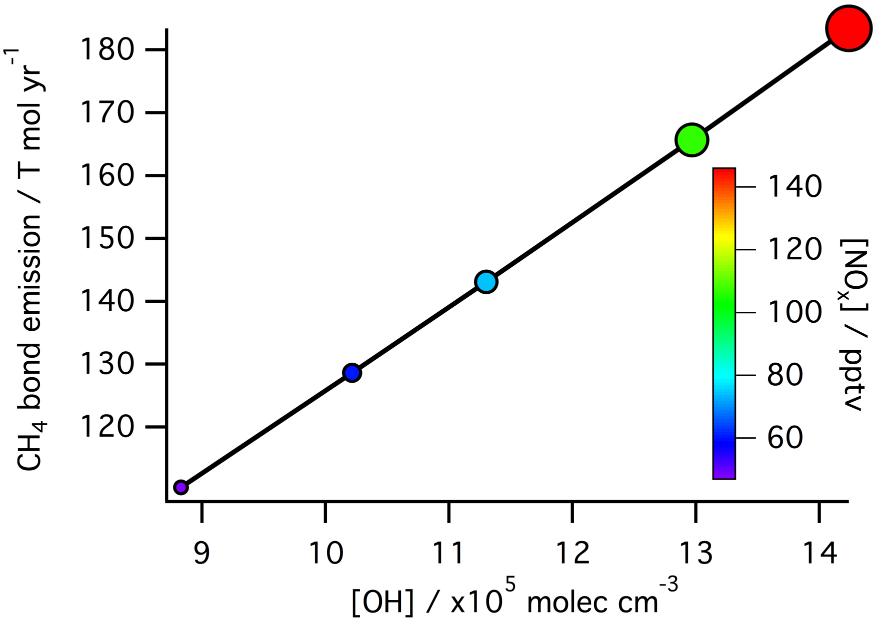

Fig. 1. Figure 7. Effective CH4 emissions as a function of global mean OH concentration, for simulations where NOx emissions were changed. Marker size and colour indicate global NOx concentration.

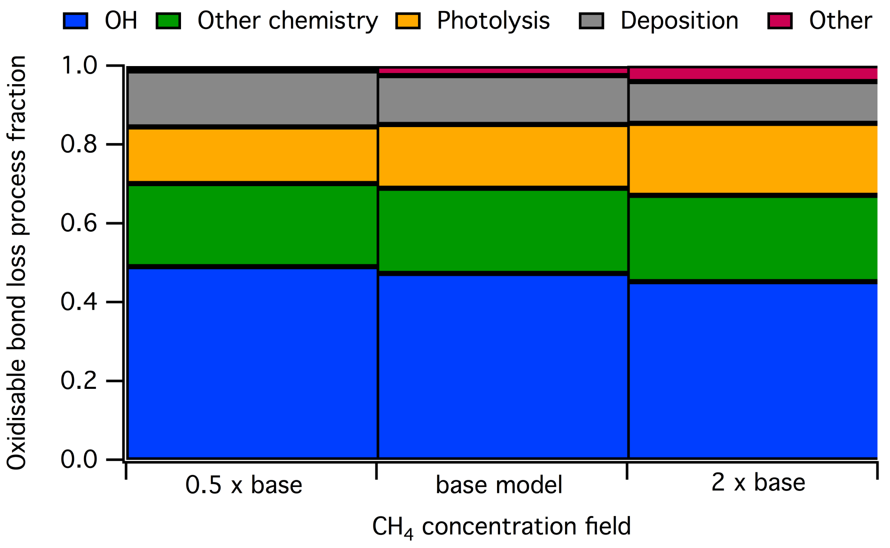

Fig. 2. Figure 8. Oxidisable bond loss mechanism fractions under changing effective CH4 emissions (0.5 x CH4 concentration field, base simulation and 2 x CH4 concentration field).

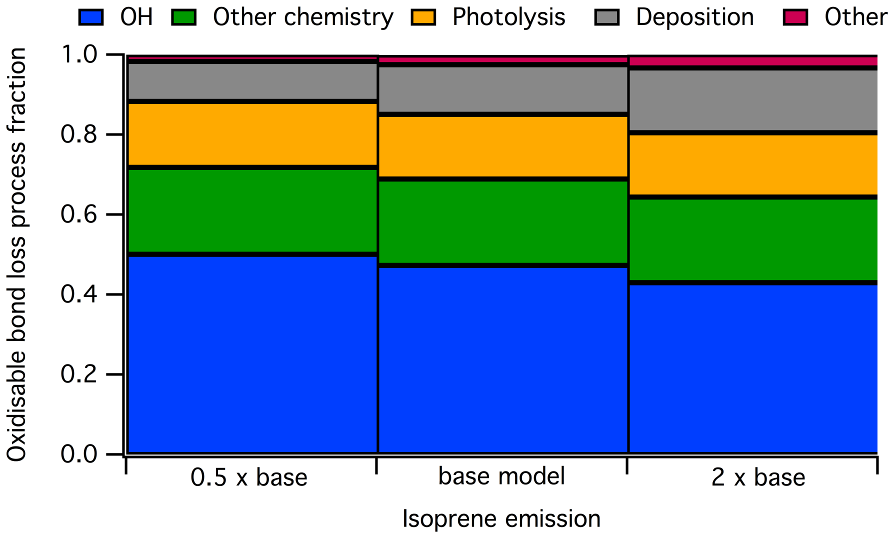

Fig. 3. Figure 10. Oxidisable bond loss mechanism fractions under changing isoprene emissions.