

# ***Interactive comment on “Assessing the sensitivity of the hydroxyl radical to model biases in composition and temperature using a single-column photochemical model for Lauder, New Zealand” by L. López-Comí et al.***

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We thank the reviewer for his/her thoughtful comments. The reviewer's comments are repeated below in italics.

*The authors report a study of the effects on OH of constraining model calculations to observations of ozone photolysis rates and concentrations of ozone, water vapour, CO and methane, as opposed to model derived fields for these variables. The model used is a single column photochemical model, based on the NIWA-UKCA model, and enables a focus on the model chemistry owing to removal of transport and physical*

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*processes whilst also demonstrating changes in chemical effects on OH as a function of altitude.*

*My major comment with the paper regards a lack of detail, and insufficient attention given to the wider applicability of the results obtained in Lauder, New Zealand, to global chemistry-climate modelling.*

We are now providing significantly more detail, improving the presentation of the results, and have also expanded the conclusions section in response to the reviewer's concern about insufficient coverage of the wider significance of the research.

1. *Abstract: The general trends for changes in OH are described but these should be quantified throughout.*

We have modified the abstract trying to strike a balance between giving some quantitative information and not overloading it with numbers which can make the abstract unreadable. This was also in response to a comment by the 2nd reviewer.

2. *Introduction: The introduction is rather short and lacking in detail. The rationale for studying OH is brief, and the paper would benefit from an expanded discussion of why it is such an important model target. The statement that 'considerable disagreement among . . . models' should be quantified, and given that the abstract describes the possibility of this work explaining 'differences in simulated OH between global chemistry models and relative to observations' some discussion of relevant previous studies is warranted. Differences in model outputs observed in intercomparisons such as ACCMIP could be of interest here, and would help place this paper and its results in greater context of previous work.*

We have now considerably expanded the introduction, giving quantitative information on the disagreement e.g. found in ACCMIP models. We hope that this addresses the reviewer's concern.

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3. *The Emmerson et al. papers referenced (line 47) refer to box models, some reference to single-column models, and examples of their use, should be given. There is no reference given for Lauder being 'known for its clean air' (line 49), or much detail given the 'large diversity of available measurements' (line 50). Apart from O<sub>3</sub>, H<sub>2</sub>O, CO, and CH<sub>4</sub>, what species are measured? Are there measurements of NO<sub>x</sub> (what are the average values?) or other VOCs?*

References to single-column models have been added in the text, as well as their different applications. Single-column models for OH chemistry, other than our own, to our understanding do not exist. The paper now states that the Emmerson et al. papers refer to the development and application of box models, rather than SCMs. See paragraph 4 of the introduction.

A reference attributing Lauder to be a clean air site has been added.

In addition to the measurements used here, Lauder produces measurements of total-column NO<sub>2</sub>, total-column BrO, and FTS measurements of a variety of species (mostly as total columns) that are reported at NDACC. For this study, relatively high-resolution profile information is needed which in the troposphere is only achieved by the ozone sondes (which produce O<sub>3</sub>, H<sub>2</sub>O, and *T* profiles). Near-surface NO<sub>2</sub> has only been measured episodically at Lauder; its abundance has generally been at or near the detection limit. We don't know what the averages would be. These measurements are unsuitable to constrain the SCM with. Lauder is well known for its total-column NO<sub>2</sub> measurements but these are dominated by a stratospheric contribution and cannot be used to infer tropospheric abundances of NO<sub>2</sub>.

A few VOCs have been derived as total-columns from FTS measurements (C<sub>2</sub>H<sub>6</sub>, HCHO, HCN, CH<sub>3</sub>OH). These species are all orders of magnitude less abundant than CH<sub>4</sub>, and biases in them would have a small direct impact on OH. For HCHO, there is a considerable discrepancy between modelled and measured total columns, which we cannot fully explain (Zeng et al., 2015) and which may

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be indicative of a knowledge gap regarding VOCs at Lauder. A more exhaustive discussion of this is however beyond the scope of this paper.

4. *Line 173: Please clarify that the changes in modelled  $O_3$  (Fig. 2a) are a result of constraining to the observations and not a model result. Is there any explanation for the increases in spring and decreases in autumn compared to the reference simulation? Or for the altitude dependence?*

In subsection 3.1 (OH sensitivity to  $O_3$  biases), paragraph 2, we now clarify that the  $O_3$  difference (fig. 2a) is indeed NIWA-UKCA ozone versus ozonesonde data. The caption of fig. 2a is also changed accordingly.

Exploring the causes of the ozone and temperature biases in NIWA-UKCA is the subject of an ongoing investigation; we don't fully understand why these biases occur either. Exploring these causes is beyond the scope of this paper; here we focus only on the consequences of these biases for OH.

5. *Line 181: Is the 5% increase an average value over all altitudes/seasons? Please clarify.*

We now clarify that this pertains only to the spring season and the altitude range of 2-6 km. 5% is about the maximum difference.

6. *Line 185: The statement that the increases in OH are the result of increases in  $j_{O1D}$  seems rather obvious given that this is the only parameter that has been changed.*

We have rephrased this sentence. Indeed there is no surprise here, but we have gained a simple quantification of the impact of TCO errors on OH.

7. *Line 188: Please explain (and discuss) more clearly what you mean by the statement that the magnitudes of the kinetics and photolysis effects are comparable. Figures 2c and 2d show the changes to  $j_{O1D}$  and OH respectively, how do these*

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*suggest anything about the  $O_3$  bias? The values shown in Figures 2a and 2b, which do correspond to the kinetics effects, are not comparable or similar to those in Figures 2c and 2d.*

The text now makes this clearer. Indeed the patterns are different, but the ranges of values are comparable.

8. *Line 193: What is the significance of a near exponential relationship? Does it have a physical basis? From the plot it is not clear that there is a near exponential relationship, if there is and it is significant, please show it on the plot and give the parameters describing the relationship. Does Figure 3 show data from all altitudes? The discussion comments on an altitude of 6 km, how does this relate to the data shown in the figure?*

The near-exponential is motivated by the Lambert-Beer Law, which links attenuation to optical thickness. The finding is still semi-empirical because the solar UV light is not monochromatic and the optical thickness of ozone is wavelength dependent. The plot only shows how OH would respond to a systematic change of the SCO. We now provide empirical fits in all three panels. In the case of SCO versus  $j_{O1D}$ , we account for the curvature by fitting a parabola to  $\log j_{O1D}$ . The fit parameters are stated in the panels, and some text is added to this effect.

9. *Line 199: Again, explain the significance of the exponential relationship and give the parameters describing it.*

The same as above.

10. *Line 213: The percentages given in the discussion are given as fractions in the figures, please change one or the other for consistency.*

We have changed the text to make it consistent with the panels.

11. *Line 235: What is the fraction of the total OH loss to  $CH_4$  and CO in the model? It is not clear from the discussion what fraction of the total OH loss occurs due*

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to reactions with  $\text{CH}_4$  and  $\text{CO}$ , what are the implications of the presence of other species, and thus the applicability of the results obtained in this work to more polluted regions. The  $\text{OH}$  concentrations shown in Figure 3 seem particularly high.

Unfortunately we cannot straightforwardly diagnose in the SCM what the fraction of  $\text{OH}$  lost to  $\text{CH}_4$  or  $\text{CO}$  is. For NIWA-UKCA, such diagnoses exist for the global domain. In the troposphere,  $\text{OH} + \text{CO}$  is the leading sink process, but this reaction does not change  $\text{HO}_x$ , and  $\text{OH}$  is well buffered w.r.t. changes in  $\text{CO}$ . For  $\text{HO}_x$ , the dominant sink processes are self-reactions of  $\text{HO}_x$  ( $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$ ,  $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O}$ ) competing with  $\text{OH} + \text{CH}_4$ . However, the methane impact is complicated by the oxidation products. In short: a satisfying answer to this question would require a much more comprehensive investigation.

Regarding the high values of  $\text{OH}$  in figure 3, again this is for the 6 km level (where  $\text{OH}$  concentrations are larger than at the surface). We have made this explicit in the figure caption.

12. *If the  $\text{CH}_4$  observations are different from the reference simulation by only  $\sim 2\%$  please explain the reported 40% sensitivity of  $\text{OH}$  to the change in  $\text{CH}_4$ . The discussion refers to the percentage changes in  $\text{OH}$  shown in Figure 6e/6f, but these do not show percentage changes. The discussion should be consistent with the figures in terms of the way the differences are expressed. Please provide some discussion of the use of  $d \ln(\text{OH})/d \ln(\text{CH}_4)$  (or  $\text{CO}$ ) in Figure 6.*

The number of 0.4 was an error.  $\text{OH}$  increases by  $> 0.6\%$  when  $\text{CH}_4$  is increased by 2% in March (figure 6c). The relative sensitivity  $A_{\text{CH}_4} = \partial \ln \text{OH} / \partial \ln \text{CH}_4$  is no longer expressed in percent. It maximizes, in absolute terms, at  $-0.32$  (meaning the relative response of  $\text{OH}$  is up to 0.32 times the relative difference in  $\text{CH}_4$ , but opposite in direction). Regarding the use of the infinitesimal notation, this is just a straightforward reformulation of equation 2. This is now made explicit in the text.

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13. *Line 275: Is  $\text{OH} + \text{CH}_4$  the dominant OH sink in the model? What is the change in the kinetics of the reaction for the temperature change applied to the model?*

The reaction coefficient for  $\text{OH} + \text{CH}_4$  in the model is  $1.85 \cdot 10^{-12} \exp(-1690/T)$ . This makes it one of the most temperature-sensitive reactions in the NIWA-UKCA chemistry scheme. The sensitivity of the reaction coefficient, at 290 K, evaluates to approximately 2%/K of temperature difference. This combined with the important role of  $\text{CH}_4 + \text{OH}$  as a  $\text{HO}_x$  sink, means that indeed  $\text{CH}_4 + \text{OH}$  plays a major role in explaining the relatively small impact of temperature changes on OH. This is now made explicit in the text.

14. *Line 310: What is the significance of this equation? Can it be applied to other models? Can values for the parameters be tabulated for various altitudes (or can altitude dependent parameters be given?). How valid is the assumption that the OH response is linear to changes in the forcings? As stated, Figure 8c suggests this is not a valid assumption.*

This equation represents a working assumption; this is now made explicit in the text. We agree that there are some non-linearities, and the assumption of linearity is not perfect, but linearity explains almost the whole pattern in Figure 8 a. Other models that focus on global and background chemistry might well behave in ways similar to our model, but we haven't tested this.

15. *Line 385: Please give some examples (and references!) of underestimated  $\text{CH}_4$  lifetimes by NIWA-UKCA and comparisons with other accepted estimates. An expanded introduction will help with this.*

In the REF-C1 simulation of NIWA-UKCA used here, the  $\text{CH}_4$  lifetime evaluates to 7.6 years. This compares to 9.2 years as the best estimate from SPARC (2013). We have added text (in section 3.5) quantifying the  $\text{CH}_4$  lifetime in NIWA-UKCA and giving this best estimate. Further citations are added in the conclusions section.

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16. *Minor comments: Line 11: 'Its impact. . .', please change this to 'The impact of O<sub>3</sub> . . .' for clarity.*

Done

17. *Line 32: 'in-situ' to 'in situ'.*

Done, also elsewhere.

18. *Line 60: Please spell out NIWA in full.*

Done

19. *Line 71/line 135: What determines the concentrations of these species in the model if there are no emissions? Are they constrained to observations? Set to zero?*

NIWA-UKCA model data are used for these species. This is now made explicit in the text (also in section 2.3).

20. *Page 101: 'Vertically integrated ozone produced here' – please reword, do you mean 'produced in this way'?*

We have changed 'vertically integrated ozone produced here' for 'the vertical integration of the observed O<sub>3</sub> profiles'.

21. *Line 161: Please replace 'a' and 'b' with 'k' in keeping with convention, and label the different 'k' appropriately to distinguish between reactions (i.e.  $k_a$ ,  $k_b$  or  $k_1$ ,  $k_2$ ).*

Done

22. *Line 290: Space in '5K'.*

Done

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23. *Line 329: 'sky' to 'skies'.*

Done

24. *Line 336: Please change the word 'combinedly'.*

We replace this with 'in combination'.

25. *Line 373: Please change 'chemical equilibrium' to 'chemical steady state'.*

Done

26. *Figure 1: Panel e, please remove the degree symbol.*

Done

27. *Figure 2: Panel f, presumably this should refer to panels 2b and 2d?*

Done

28. *Figure 3: Please remove the titles to the plots and leave just the labels a, b and c. See comments above regarding the exponential relationships - please give the parameters (and fit statistics) for the relationships described if these are important. If they are, why mention them?*

Done. We now state the fitting parameters, but we don't regard the fit statistics as necessary in this context as these coefficients are not used any further in the following text.

29. *Figure 4: The data shown in the plots are given as percentages in the discussion. Please see comments above regarding consistency.*

Changes of species are generally now given as percentages relative to the reference, but sensitivity coefficients are given as fractions. We think this is now handled consistently.

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30. *Figure 5: Please clarify in the caption that panels e and f refer to plots a & b and c & d, respectively. The analysis  $d \ln(OH)/d \ln(H_2O)$  is not explicitly referred to in the text (likewise for Figure 6).*

We have clarified the caption and have removed the formula.

31. *Figure 6: Figure 6e in the caption is referred to as Figure 6d.*

Changed. We have reformulated the caption along the same lines as figure 5.

32. *Figure 8: Panel c, please explain the significance of the dashed and red lines.*

The significance of the red solid and black dashed lines has been explained in the caption of Figure 8.

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