

Major Points:

1. *There are a number of problems in the way the MLS data are presented and used. First, it is not clear that the day-night differences are being used for the “standard” HO₂ product, as recommended in validation papers and in MLS data quality documents. This is critical since HO₂ is a major focus for the paper. Second, there is no mention of the version of the data used (v3.3?) and whether all of the appropriate data screens were used. Third, all of the figures show data and profiles to 0.01 hPa, when in fact the useful range for HO₂ is clearly stated at 0.046 hPa, and for O₃ at 0.02 hPa. Data above these levels are not recommended for science purposes and should not be part of the analysis. This paper would clearly benefit from some interaction and discussion with members of the MLS team to ensure that the data are being applied correctly.*

We agree with this comment. In the revised manuscript the following corrections are made (see lines 322-333):

- (1) We have used the day-minus-night differences for the HO₂ product. Accordingly, the results presented in Figs. 2–6 have been completely recalculated.
- (2) The information on the MLS data version in use, i.e. v4.2, the latest one, have been added. All the data screens were applied when dealing with the MLS standard product.
- (3) We have limited our analysis to the 1–0.046 mbar pressure interval where all data are suitable for scientific use, as prescribed by (Wang et al., 2015; Livesey et. al., 2017).

2. *The connection between the CTM results and the analytic formulation is not sufficiently explored. Figure 1 is used to show that the difference between the CTM and equilibrium equation is a few percent or less, and that this justifies the use of the analytic formulation in the subsequent statistical evaluation. However, there is not enough information given about the CTM to judge whether or not this is really an independent validation. Presumably, the CTM uses the same set of reactions and the same equilibrium assumptions along with the “family” chemical species approach, so it is not surprising that they agree. It is also not clear whether the CTM also includes NO_x chemistry, which might have an impact in the upper stratosphere and lower mesosphere.*

We agree that the original version of the manuscript contained little information about the 3D chemical transport model (CTM). Indeed, our model uses a family concept by Shimazaki (Shimazaki, 1985). It is used to calculate the evolution of the components of

HO_x and NO_x families, while the O_x family is calculated via regular implicit Euler method. Moreover, it should be emphasized that the Shimazaki scheme utilizes an implicit Euler scheme too and does not use the steady state approximation for short-lived components. Thus, in calculating the evolution of OH, HO₂, and O₃ within the framework of the CTM, we *do not use* the photochemical equilibrium condition.

In the revised manuscript the following changes have been made:

(1) A list of reactions, accounted for by the CTM, is added (see Table 1). It can be seen first of all, that the CTM includes comprehensive NO_x chemistry. Secondly, the complete set of reactions (63 in total) is much bigger than the one we consider to describe the daytime balance of OH, HO₂, and O₃ concentrations. In the original manuscript there were 9 of them — now there are 8, the reaction $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ was removed. Our numerical analysis showed that its contribution to the analytic expression $F(\text{OH}, \text{HO}_2, \text{O}_3) = 1$ is less than 1%.

(2) The description of the chemical transport model, including its dynamics and the integration methods used, is substantially expanded (see lines 167-195). In particular, it is stated that «The evolution of the components of HO_x (H, OH, HO₂, H₂O₂) and NO_x (N, NO, NO₂, NO₃) families is calculated using the chemical family concept proposed by Shimazaki (Shimazaki, 1985). This is done because of the presence of short-lived components among these families, with lifetimes much shorter than those of the families themselves, which imposes significant restrictions on the value of the CTM's integration step. For example, the daytime lifetimes of OH and HO₂ above 70 km are about 1 s or less, while the lifetime of the HO_x family is about 10⁴ s or more. Therefore, when calculating these components individually it is necessary to set the CTM's integration step to be much less than 1 s. In our work, the Shimazaki technique is applied for calculating the evolution of each component of the HO_x and NO_x families. We emphasize that this technique does not explicitly use the steady-state approximation for the components, instead it utilizes the approach based on an implicit Euler scheme (see Shimazaki, 1985). This allows increasing the integration step of CTM significantly without loss of accuracy of calculating the short-lived components. In our work the integration time is chosen to be 9 s.»

As a further example, there are known effects on HO_x and NO_x in the mesosphere from energetic particle precipitation events [e.g. many papers by Jackman et al and Verronen et al], and it would be important for the CTM to include these if it is intended to be used as a validation of the equilibrium expression. In fact, Figures 2 and 3 display data from January

2005, during a period with a documented SPE event [Jackman et al., ACP, 2011]. The possible influence of SPE perturbations needs to be discussed and addressed.

Done. We carried out a brief analysis of the possible effect of solar proton events (SPE), which were not implemented in the CTM, on the mesospheric photochemistry in daytime. We considered the most prominent impact of SPE in the context of the problem: the impact on the chemical balance of OH. Comparing the additional OH source due to SPE with the main source of this component (via the reactions $\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$, $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$ and $\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$) we showed that the influence of SPE on the daytime balance of OH is insignificant.

We made two additions to the revised manuscript:

(1) a new figure (see Fig. 2);

(2) the following text (see lines 251-256, 263-275):

«Note also that Eq. (1) and Eq. (6) take into account only the main daytime source of OH (P_{OH}) specified by reactions R18, R14, and R21:

$$P_{\text{OH}} = k_{18} \cdot \text{HO}_2 \cdot \text{O} + 2k_{14} \cdot \text{HO}_2 \cdot \text{H} + k_{21} \cdot \text{O}_3 \cdot \text{H}$$

These reactions run “inside” the HOx (H, OH, HO₂, H₂O₂) family and do not perturb its total concentration. The height–latitude cross-sections of $\langle P_{\text{OH}} \rangle$ for each month are presented in Fig. 2.

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Another source of OH is sporadically activated during charged particle precipitation events and exists for a relatively short time (several days). Solar proton events (SPE) perturb the ionic composition in the mesosphere and the upper stratosphere considerably and trigger a whole cascade of reactions involving ions, neutral components and their clusters (e.g., $\text{O}_2^+ \cdot \text{H}_2\text{O}$). This leads to an additional (to reactions R59 and R7) conversion of H₂O molecules into OH and H (Solomon et al., 1981). The maximum of the OH production rate ($P_{\text{OH}}^{\text{SPE}}$) induced by SPE is located in the polar latitudes in the region of 60–80 km and, as a rule, does not exceed $2 \cdot 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ (Jackman et al., 2011, 2014). It can be seen from Fig. 2 that at these latitudes and altitudes the $P_{\text{OH}}^{\text{SPE}} / P_{\text{OH}}$ ratio does not exceed 1-2%, even for the maximum values of $P_{\text{OH}}^{\text{SPE}}$. This means that the impact of $P_{\text{OH}}^{\text{SPE}}$ on Eq. (6) is of the same order of smallness as in the case of reactions R59 and R7, hence, it may be neglected. A similar conclusion can be made for other reactions from Table 1, not accounted for by Eq. (6), including the ones involving NO_x in both quiet and perturbed conditions in the mesosphere.»

(3) We found the mistake in Fig. 1 below 50 km caused by the use of improper computer number format (float32 instead of float64). So Fig.1 was recalculated and redrawn. The value of $\langle F \rangle$ below 50 km increases.

If the CTM includes a comprehensive simulation of all known reactions and processes impacting HO_x, and there is still agreement with the analytic approach, then the results are more credible. The paper should demonstrate that in fact the CTM provides a complete description of HO_x photochemistry.

Done. To sum up, the following corrections have been made:

- (1) A list of reactions is added, accounted for by the CTM. It can be seen that the CTM includes complete chemistry of the mesosphere.
- (2) The description of the chemical transport model is substantially expanded in the part relating to dynamics and the methods of integration applied.
- (3) Analysis of the possible effect of solar proton events (SPE), which are not implemented in our model, on the photochemistry in the daytime mesosphere is carried out.

Finally, there is a problem with converting pressure altitudes in the model to pressures by assuming a constant scale height of 7 km. This assumption can lead to offsets of 1 km or larger and is particularly critical when comparing vertical profiles with large gradients. For example, at 62 km the US std atmosphere has a pressure of 0.1671 mb. If a constant 7-km scale height is used in the expression in the paper, one would calculate $p=0.1442$ at 62 km. The analysis in this paper should use the temperatures in the model to compute convert altitude to pressure using hydrostatic equilibrium on a layer-by-layer basis.

Done. In the revised manuscript, the pseudo-height scale was replaced by pressure levels (see lines 199-202 and Figs 1-3). In addition, we indicated the approximate heights in km which were calculated for a given month utilizing averaged temperature profiles of the model and hydrostatic equilibrium.

3. There is not enough detail on the conclusion that the offline HO₂ product better agrees with the statistical retrieval. First, there is no direct comparison between the offline product and the statistical retrieval, as there is for the standard product and the statistical retrieval (figs 4-6). There is only a presentation of the offline HO₂ product, and the reader has to refer back to figs 4-6 and then estimate just how much better the agreement really is. The improvement needs to be quantified more directly. Also, there is no discussion as to why the agreement is better and this really gets down to the science. Does this paper intend to

suggest that the offline HO₂ product is superior to the standard product? If so, then the discussion/conclusion needs to be expanded to clearly justify why this is so. There also needs to be some explanation for why the offline product is different in the first place, without forcing to reader to go back and review the Milan et al [2015] paper.

Done. First of all, the description of the offline HO₂ retrieval is expanded and its advantages over the standard MLS product are pointed out (see lines 395-403):

«Moreover, new data on the HO₂ distributions were recently obtained from the MLS measurements. Millán et al. (2015) performed the offline retrieval of daily zonal means of HO₂ profiles using averaged MLS radiances measured in 10° latitude bins. Averaged spectra have a better signal to noise ratio, which removes many of the limitations of the MLS standard product for HO₂. In particular, the upper boundary of the altitude region in which daytime data is suitable for scientific use has reached 0.0032 mbar, and the "day-minus-night" correction is not needed at altitudes above 1 mbar. Comparison with various experimental and model data has shown that the offline retrieval reproduces the basic properties of the HO₂ distribution in the mesosphere relatively well (at least qualitatively) (Millán et al. 2015).»

Second, we made a direct comparison (see Fig. 10) of the offline MLS product with the results of our statistical retrieval and the standard product of MLS. One can see from Fig. 10 that our results better match the offline product than the standard one. The most noticeable difference is in the location of the mesospheric maximum of the HO₂ concentration. According to the standard product it is close to 0.1 mbar, while the retrieved data and the offline product demonstrate the altitudes above 0.046 mbar. This is also confirmed by the HO₂ distributions calculated using our 3D chemical transport model (see lines 391-394 and Fig. 9), In the revision we highlighted (see lines) that the higher location of that maximum in the results of the of HO₂ statistical retrieval is due to the influence of MLS data on OH, which have the mesospheric maximum (see Figs. 6–8) also well above 0.1 mbar.

Minor Points:

The grammar and wording is awkward or incorrect in a number of places, for example Abstract: "statistically correct approach" is not illuminating. One would not expect ACP to publish a "statistically incorrect approach". Suggest a "Bayesian statistical approach".

Corrected. "statistically correct approach" was replaced by "statistical approach" everywhere in text. See lines 14, 135.

“air concentration” is more generally “neutral density”,

Corrected. “air concentration” was replaced by “neutral density” everywhere in text. See lines 19, 141.

“air temperature” is generally just “temperature”.

Corrected. “air temperature” was replaced by “temperature” everywhere in text. See lines 19, 141, 323.

*“We have performed *a* one-year simulation”.*

Corrected. See line 20.

Last sentence is unclear. Also “MLS primary data”, what is primary data? Perhaps this should be MLS radiances.

Corrected. See lines 29-30.

In terms of the reaction sets, there appears to be a gaping omission of the HOx production reactions, H₂O+hν and H₂O+O(1D). These should be included for completeness; however, I suspect their terms may drop out when forming the ratio OH/HO₂.

Done. We have directly compared the source of OH ($P_{OH}^{H_2O}$) due to the reactions $H_2O+h\nu \rightarrow H+OH$ and $O(^1D)+H_2O \rightarrow 2OH$ with the main source of that component, P_{OH} , via the reactions $HO_2 + O \rightarrow OH + O_2$, $H + O_3 \rightarrow OH + O_2$ and $H + HO_2 \rightarrow 2OH$. The ratio $P_{OH}^{H_2O} / P_{OH}$ does not exceed 3-4%.

Two corrections are made in the revised manuscript:

(1) new figures are added (Fig. 2-3);

(2) the following text is inserted (lines 251-262):

«Note also that Eq. (1) and Eq. (6) take into account only the main daytime source of OH (P_{OH}) specified by reactions R18, R14, and R21:

$$P_{OH}=k_{18} \cdot HO_2 \cdot O + 2k_{14} \cdot HO_2 \cdot H + k_{21} \cdot O_3 \cdot H$$

These reactions run “inside” the HO_x (H, OH, HO₂, H₂O₂) family and do not perturb its total concentration. The height–latitude cross-sections of $\langle P_{OH} \rangle$ for each month are presented in Fig. 2.

The next important daytime source of OH is specified by reactions R59 and R7 involving H₂O, the main source for the HO_x family:

$$P_{OH}^{H_2O} = (k_{59} + 2 \cdot k_7 \cdot O(^1D)) \cdot H_2O$$

Figure 3 shows height–latitude cross-sections of $\langle P_{OH}^{H_2O} / P_{OH} \rangle$ for each month. Comparing Fig. 1 and Fig. 3, we conclude that the previously indicated 3–4 % deviation of $\langle F \rangle$ from 1 in the region between 76 km and 86 km is largely due to the neglect of these reactions.»

When deriving equation 14, which forms a major basis for the paper, I was not able to reproduce the authors' results and cannot comment on the validity of this result. It seems much more complicated than the text would suggest. I strongly recommend an appendix which details the step-by-step process at arriving at equation 14.

The whole section (Sec.2) was rewritten at the price of an insignificant increase in volume. Including, all the steps needed to derive the equation $F(OH, HO_2, O_3) = 1$ are presented. We believe that in this form this section harmoniously fits into the main canvas.

Figure 3 is unclear what ranges of latitudes are being shown.

Corrected. See Fig. 5.

Figs 4-6 contain horizontal dotted lines but these are not explained in the text or caption.

This horizontal dotted lines marked the upper limit of air pressure (0.046 mbar) where HO₂ data are suitable for scientific use. In the revised manuscript we restricted the pressure range by 0.046 mbar.