

Dear Editor,

We would like to say many thanks the Referee for taking the time to review our manuscript and providing valuable recommendations. Their constructive criticism made the work clearer and more precise. We took into account all the remarks of Referee and, to the best of our ability, implemented the corresponding changes in the manuscript.

In the following, we address the comments point by point and show how the manuscript has been changed according to the comments. Below we use a certain color notation: comments by Referee are in red, our responses are in black, and the changes in the manuscript are in blue (placed inside the quotation marks).

Response to the comments on the paper by Referee 1

General Comments

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I am not clear on what significant new knowledge is gained. Some of the conclusions seem unsubstantiated and even unrealistic, especially the main conclusion that “the simultaneous application of OH and HO₂ equilibrium to the SABER data (O₃, volume emission rates at 2.0 and 1.6 μm) together with the criteria (16) and (24) to control this equilibrium validity is going to retrieve all unknown HO_x – O_x components (O, H, OH, and HO₂), extending the altitude range of retrieval below 80 km and without external information.”

In the revised manuscript, we give the detailed explanation of the noted conclusion (see Discussion):

«The results of our paper allow modifying the Panka et al. method to extend its capabilities. The simplest development of this method seems to be the following. First of all, note that the HO₂ equilibrium condition (9) depends on H and O only and can be used within the self-consistent retrieval procedure, considering the following system of equations:

$$OH(v = 1 - 9) = \frac{k_{12} \cdot H \cdot O_3 \cdot M \cdot f(v) + \sum_{v' > v} (a_1(v', v) + a_2(v', v) \cdot O_2 + a_3(v', v) \cdot N_2 + (a_4(v', v) + a_5(v', v)) \cdot O) \cdot OH(v')}{a_6(v) \cdot O + \sum_{v' > v} (a_1(v, v') + a_2(v, v') \cdot O_2 + a_3(v, v') \cdot N_2 + (a_4(v, v') + a_5(v, v')) \cdot O)}$$

$$OH(0) = \frac{\sum_{v' > 0} (a_1(v', 0) + a_2(v', 0) \cdot O_2 + a_3(v', 0) \cdot N_2 + (a_4(v', 0) + a_5(v', 0)) \cdot O) \cdot OH(v') + k_{18} \cdot O \cdot HO_2 + 2 \cdot k_{14} \cdot H \cdot HO_2}{k_{17} \cdot O}$$

$$HO_2 = \frac{k_{20} \cdot H \cdot M \cdot O_2}{k_{18} \cdot O + (k_{14} + k_{15} + k_{16}) \cdot H}$$

$$VER_{2\mu m} = a_1(9, 7) \cdot OH(9) + a_1(8, 9) \cdot OH(8),$$

$$VER_{1.6\mu m} = a_1(5, 3) \cdot OH(5) + a_1(4, 2) \cdot OH(4),$$

where a_{1-6} are the constant rates of the processes $OH(v) \rightarrow OH(v' < v) + h\nu$, $OH(v) + O_2 \rightarrow OH(v < v') + O_2$, $OH(v) + N_2 \rightarrow OH(v < v') + N_2$, $OH(v) + O(^3P) \rightarrow OH(v' \leq v - 5) + O(^1D)$, $OH(v) + O(^3P)$

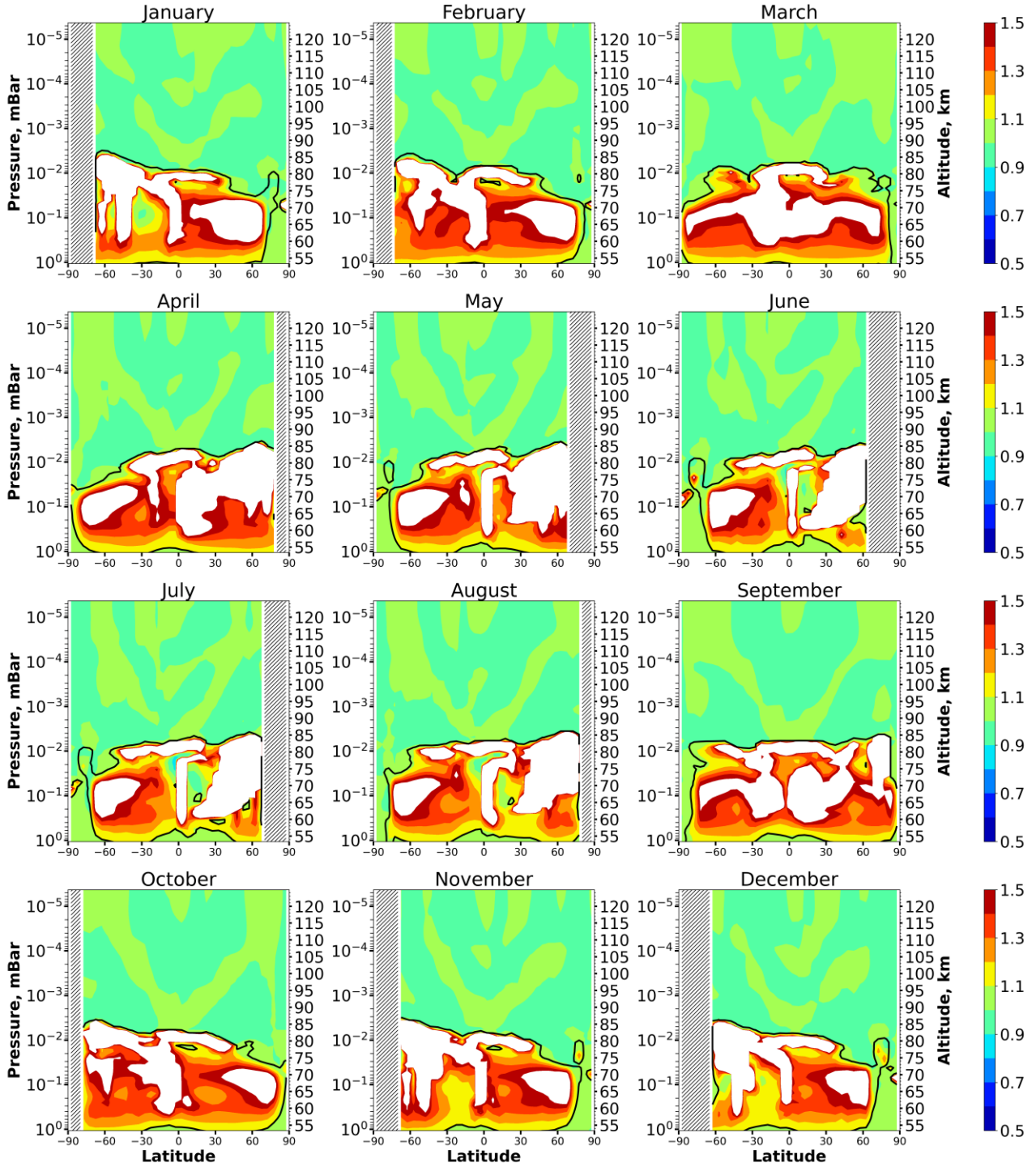
→ $\text{OH}(v' < v) + \text{O}(^3\text{P})$, and $\text{OH}(v) + \text{O}(^3\text{P}) \rightarrow \text{H} + \text{O}_2$, respectively. Note this system includes 13 equations with 13 unknown variables. Therefore, the solution to the system for a set of the SABER data (simultaneously measured profiles of O_3 , T, pressure, $VER_{2\mu\text{m}}$, and $VER_{1.6\mu\text{m}}$) gives one simultaneously retrieved profiles of O, H, $\text{OH}(v=0-9)$, and HO_2 . By applying the criteria (17) and (25) to obtained O and H profiles, we verify the fulfillment of OH and HO_2 equilibrium conditions and determine the height below which the resulting profiles should be cut. More advanced retrieval procedure would be statistical, based on Bayesian theorem, taking into account the uncertainties in measurement data and rate constants. Similar, for example, to Kulikov et al. (2018a), it should include a derivation of posterior conditional probability density function of retrieved characteristics and numerical analysis of this function. Detailed development of this retrieval method is outside of this paper and should be carried out in a separate work.»

In addition, below we address a number of issues that attracted the Referee's criticism.

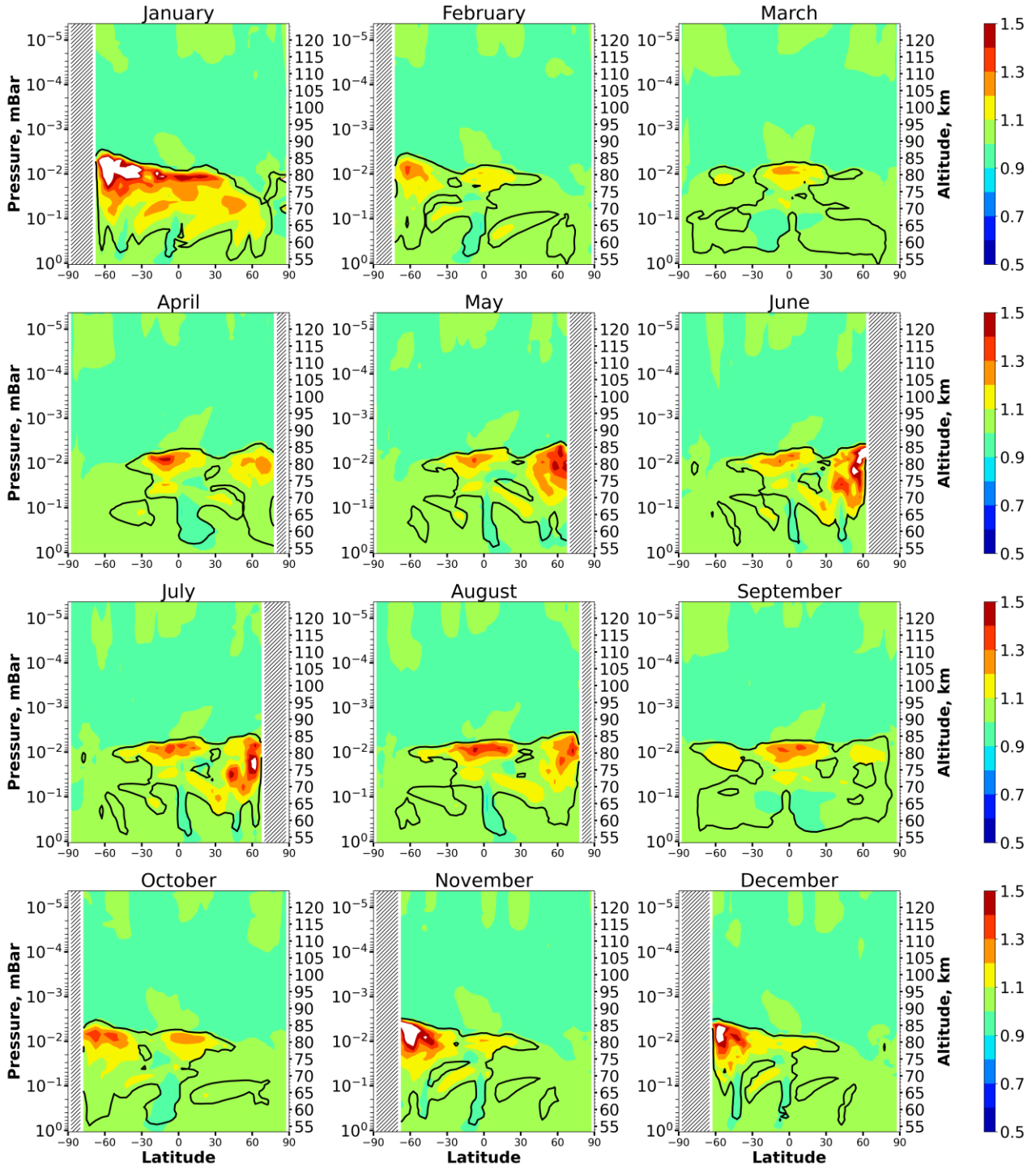
Specific Comments

* The manuscript uses solar elevation angles greater than 95° to discriminate between twilight and nighttime conditions. This is insufficient and would include twilight conditions during which steady-state nighttime conditions may not have been established yet. The convention for astronomical nighttime is 108° , and various studies have used values in the range $100-110^\circ$. In comparison, the Panka et al. (2021) SABER data set this manuscript considers indicates a nighttime cutoff angle of 105° (this is according to the available data for 2009 at the website <https://saber.gats-inc.com>, the Panka et al. (2021) paper does not explicitly call this angle).

We apologize for our mistake and the misunderstanding it caused. Actually, all Figures in the paper were plotted using the lower threshold at 105° for the nighttime solar zenith angle (SZA). Nevertheless, during the revision stage, we plotted our results using different values of the SZA threshold and found that including twilight solar zenith angles in the range ($95^\circ-105^\circ$) allows extending the latitude range of OH and HO_2 equilibrium fulfillment (see Figures below and Supplement). When OH and HO_2 equilibrium conditions are applied in retrieval of unmeasured characteristics from measurement data, this also allows including noticeable part of data into the consideration.



Nighttime mean and monthly averaged HO_2/HO_2^{eq} , where HO_2^{eq} is equilibrium concentration determined by Eq. (4). Black line shows the border of HO_2 equilibrium according to condition (1). The stippling corresponds to $\chi < 95^\circ$. The white area represents the $\langle HO_2/HO_2^{eq} \rangle$ ratio outside the $[0.5, 1.5]$ interval.



Nighttime mean and monthly averaged OH/OH^{eq} , where OH^{eq} is equilibrium concentration determined by Eq. (5). Black line shows the border of OH equilibrium according to condition (1). The stippling corresponds to $\chi < 95^\circ$. The white area represents the $\langle OH/OH^{eq} \rangle$ ratio outside the $[0.5, 1.5]$ interval.

We are grateful to Referee for valuable remark and added a few sentences in this sense in the revised manuscript (see Discussion):

«Note the presented results were plotted using the lower threshold at 105° for the nighttime solar zenith angle (χ) to exclude the twilight transition processes. Nevertheless, our additional analysis revealed that OH and HO₂ equilibrium conditions are well fulfilled at $\chi > 95^\circ$. Evidently, during the processing of the measurement data, taking twilight χ in ($95^\circ, 105^\circ$) range into account extends the latitude range of OH and HO₂ equilibrium application and includes noticeable part of data into the consideration. However, in this case, one should check for additional condition (Kulikov et al., 2023a):

$$e^{\int_{lt_{bn}}^{lt} \tau_{HO_2}^{-1} dt} \gg 1, e^{\int_{lt_{bn}}^{lt} \tau_{OH}^{-1} dt} \gg 1, \quad (27)$$

where τ_{HO_2} and τ_{OH} are the HO₂ and OH lifetimes determined by Eqs. (11) and (19), lt is local time of data, lt_{bn} is the local time at the beginning of the night. Note that at night, O and H tends to decrease due to the shutdown of the O_x and HO_x family photochemical sources. Thus, analyzing the measurement data, one can apply a more stringent conditions:

$$e^{\frac{lt-lt_{bn}}{\tau_{HO_2}}} \gg 1, e^{\frac{lt-lt_{bn}}{\tau_{OH}}} \gg 1. \quad (28)»$$

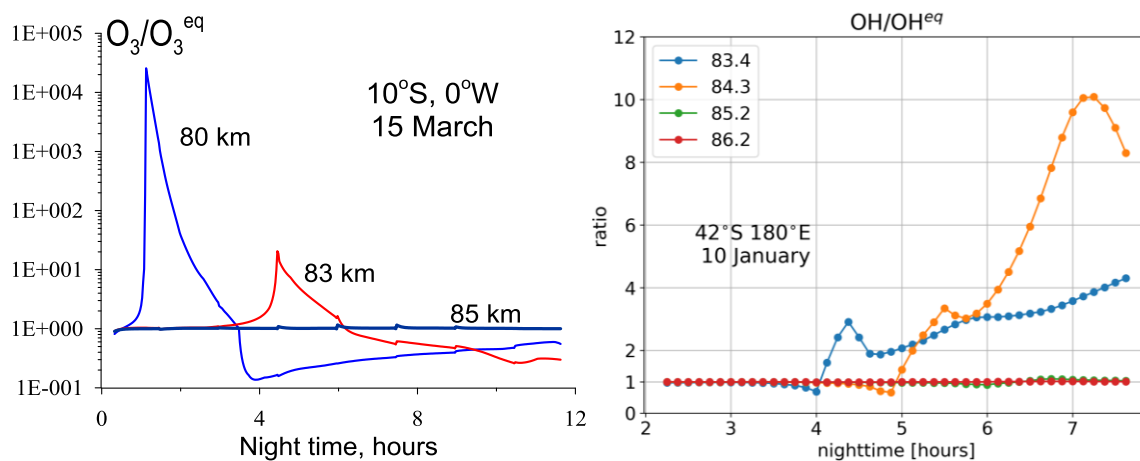
Also, note that 95° χ threshold was used in other papers. Please see, for example, Mlynchak et al. (JGR, 2013, <https://doi.org/10.1002/jgrd.50401>) and Mlynchak et al. (JGR, 2014, <https://doi.org/10.1002/2013JD021263>), where the nighttime ozone equilibrium condition was applied for O and H retrieval from SABER data. The Referee remark is more important for ozone, because its equilibrium concentration jumps at sunset due to the shutdown of O₃ photodissociation. Nevertheless, Kulikov et al. (ASR, 2023, <https://doi.org/10.1016/j.asr.2022.11.005>) confirmed using the SABER data that $\chi > 95^\circ$ cutoff is enough to exclude the ozone in transition to a new equilibrium state. In the case of OH and HO₂, the photodissociation processes are not among main sinks and sources of these components in daytime (Kulikov et al., ACP, 2018, <https://doi.org/10.5194/acp-18-7453-2018>). Moreover, usually, the OH and HO₂ lifetimes, at least, during twilight time are essentially shorter than the O₃ lifetime (Kulikov et al., ASR, 2023, <https://doi.org/10.1016/j.asr.2022.11.005>).

* The criteria for equilibrium validity conditions require a difference of less than or equal to 10% between the species concentration calculated by the chemical transport model and that estimated using instantaneous local equilibrium between production and loss. The manuscript provides no discussion of uncertainties in the model, the observations, and several rate constants at the low MLT temperatures. To have confidence that when the equilibrium criterion is not met there is a meaningful deviation from equilibrium, all the other uncertainties must be significantly smaller than

the considered range of departure from equilibrium. This does not appear to be the case given all the above uncertainties. This is a critical point that is fundamental to this research effort. The comparison with the Panka et al.(2021) data set further demonstrates this point.

The Referee remark points to a very important issue, which was regrettably omitted in the initial version of the manuscript. That could, indeed, alter the perception of scientific significance of the results obtained.

The criterion for equilibrium condition validity of a certain trace gas limits a possible difference between local values of its true (in our case, calculated value) concentration n and equilibrium concentration n^{eq} . Therefore, when equilibrium condition is applied to measurement data in the retrieval of unmeasured characteristics, the criterion allows to control and limit the possible error caused by the equilibrium approximation. Our analysis of data modeling for different trace gases shows that the ratio n/n^{eq} in nonequilibrium areas varies widely and may reach several orders of magnitude.



Examples of evolution of the ratio between local O_3 and OH concentrations and their equilibrium concentrations, respectively, obtained by the numerical simulation of the mesosphere – lower thermosphere.

Thus, without using the proposed criteria or other restrictions (for example, in height or pressure), the error in retrieved characteristics due to the use of equilibrium approximation is uncontrollable and may significantly exceed all other errors in the retrieval procedure due to uncertainties of measurement data and rate constants. In the revised manuscript, we added a few sentences in this sense in Introduction:

«The local ratio between true and equilibrium concentrations may vary widely and reach up to several orders of magnitude (e.g., Figure 5 in Kulikov et al. (2018b)). Thus, without special restrictions, the error in retrieved characteristics due to the use of equilibrium approximation is

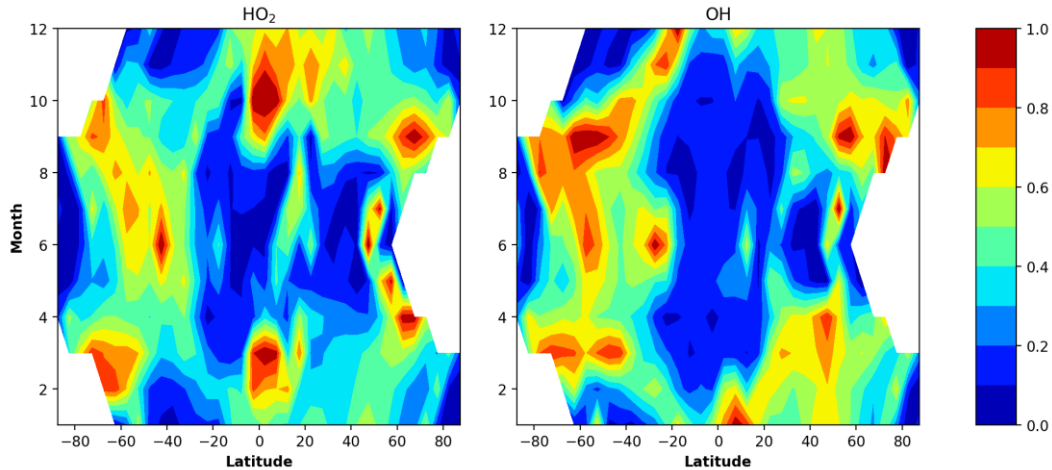
uncontrollable and may significantly exceed all other errors in the retrieval procedure due to, for example, uncertainties in the measurement data and rate constants.

.....

Note when equilibrium condition is applied to measurement data in the retrieval of unmeasured characteristics, the criterion allows controlling and limiting the possible error caused by the equilibrium approximation.»

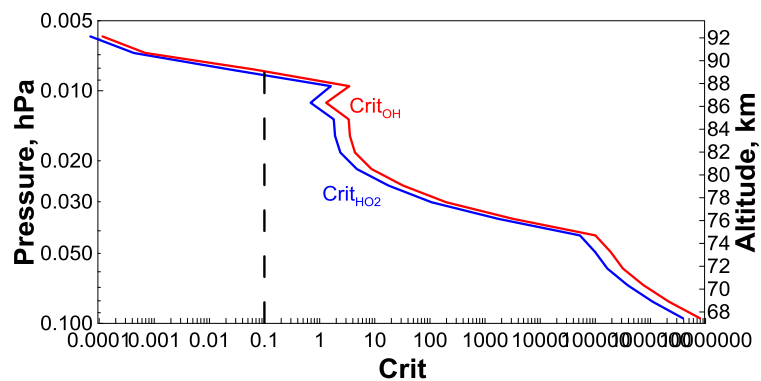
Kulikov, M. Y., Belikovich, M. V., Grygalashvyly, M., Sonnemann, G. R., Ermakova, T. S., Nechaev, A. A., and Feigin, A. M.: Nighttime ozone chemical equilibrium in the mesopause region. *J. Geophys. Res.*, 123, 3228–3242, <https://doi.org/10.1002/2017JD026717>, 2018b.

Moreover, following the Referee remark, we estimated the sensitivity of the presented HO₂ and OH criteria ($Crit_{HO_2}$ and $Crit_{OH}$) to the uncertainties of characteristics involving in the expressions of these criteria (in the revised manuscript, the conditions (17) and (25)). The local heights of the OH and HO₂ equilibrium borders ($z_{HO_2}^{crit}$ and z_{OH}^{crit}) according to the criteria are determined as the altitudes at which $Crit_{HO_2} = 0.1$ and $Crit_{OH} = 0.1$, respectively. We considered the whole dataset of nighttime profiles obtained by the numerical simulation of a one-year global evolution of mesosphere – lower thermosphere and evaluated total uncertainties to determination of $z_{HO_2}^{crit}$ and z_{OH}^{crit} from each local (in time and space) dataset (profiles of O, H, O₃, M, O₂, and temperature). Following the typical analysis presented, for example, in Mlynchak et al. (JGR, 2013a, 2014), each uncertainty was calculated as a root sum square of the sensitivities to the individual perturbations of certain variables or parameters in the expressions (17) and (25). The following uncertainties for the variables were used: 5K in the temperature and 30% in O₃, O, and H. The uncertainties in rate constants with their temperature dependencies were taken from Burkholder et al. (2020). As the result, the monthly and longitudinally mean total uncertainties to determination of $z_{HO_2}^{crit}$ and z_{OH}^{crit} were found varying in the range 0.02-1 km, depending on altitude and season.



The monthly and longitudinally mean total uncertainties to determine the local heights of the OH and HO₂ equilibrium borders according to the criteria. The white area shows no data due to polar day.

Note these values are comparable with the typical height resolution of satellite data that allows considering our criteria as a robust instrument for equilibrium condition validity. The main reason of relatively low sensitivity of $z_{HO_2}^{crit}$ and z_{OH}^{crit} is the strong height-dependence of $Crit_{HO_2}$ and $Crit_{OH}$ near the value of 0.1.



The examples of height-dependence of $Crit_{HO_2}$ and $Crit_{OH}$.

In the revised manuscript, we added a Figure and a paragraph to address the issue (see Discussion): «We evaluated the sensitivity of the presented HO₂ and OH criteria ($Crit_{HO_2}$ and $Crit_{OH}$) to the uncertainties of characteristics involving in the expressions (17) and (25). The local heights of the OH and HO₂ equilibrium borders ($z_{HO_2}^{crit}$ and z_{OH}^{crit}) according to the criteria are determined as the altitudes at which $Crit_{HO_2} = 0.1$ and $Crit_{OH} = 0.1$, respectively. We considered the whole dataset of nighttime profiles obtained by the numerical simulation of a one-year global evolution of

mesosphere – lower thermosphere and estimated total uncertainties to determination of $z_{HO_2}^{crit}$ and z_{OH}^{crit} from each local (in time and space) dataset (profiles of O, H, O₃, M, O₂, and temperature). Following the typical analysis presented, for example, in Mlynczak et al. (2013a, 2014), each uncertainty was calculated as a root sum square of the sensitivities to the individual perturbations of certain variables or parameters in the expressions (17) and (25). The following uncertainties of the variables were used: 5K in the temperature and 30% in O₃, O, and H. The uncertainties in reaction rates and their temperature dependencies were taken from Burkholder et al. (2020). As the result (see Figure 7), the monthly and longitudinally mean total uncertainties to determination of $z_{HO_2}^{crit}$ and z_{OH}^{crit} were found varying in the range 0.02-1 km, depending on altitude and season. Note these values are comparable with the typical height resolution of satellite data that allows considering our criteria as a robust instrument for equilibrium condition validity. The main reason of relatively low sensitivity of $z_{HO_2}^{crit}$ and z_{OH}^{crit} is the strong height-dependence of $Crit_{HO_2}$ and $Crit_{OH}$ near the value of 0.1.»

* Regarding the examination of SABER remote-sensing observations and the modeling analysis by Panka et al.(2021), consideration of the relevant uncertainties would provide context and assess the results. There are substantial uncertainties in all the retrieved SABER minor constituents, [H], [O], and [O3] being the most relevant in this case. These are at best within approximately 20% and the relative errors are often largest at the lower and higher ends of the studied altitudes. With all this in mind, it seems that the data points shown in Figure 12 may well be outliers with limited significance at best. According to the manuscript (lines 406-407), “...the local height position of the OH equilibrium boundary can rise up to 87 km.” The Panka et al. data set comprises 263,432 measurements and the number of points above 80 km is no more than approximately 2% (based on about five hundred points on each of the panels of Fig. 12). The overwhelming majority of those measurements are not consistent an equilibrium height above 80 km.

The number of points in the panels of the Figure 12 relative to the total number of profiles per a month varies in the range (3.3-7.7)%, depending on the month. Moreover, as was shown above, the OH and HO₂ equilibrium borders according to the criteria demonstrate low sensitivity to the uncertainties in the variables and parameters. Nevertheless, following this remark and the remark by the Referee 3, we have excluded the OH equilibrium boundary retrieval with the Panka et al. data from revised manuscript. As pointed by the Referee 3, the main reason is the question of the correctness of the Panka et al. approach for O retrieval below 85 km, see the discussion to the Kulikov et al. (ACP, 2023), pages 7-9 in <https://egusphere.copernicus.org/preprints/2023/egusphere-2023-1046/egusphere-2023-1046-AC2-supplement.pdf>. Additional question is the correctness of the Panka et al. approach for OH retrieval

below 87 km due to unknown source of HO₂ data. Instead of the deleted analysis, we give the detailed explanation in Discussion, how the results of our paper can help modifying the Panka et al. method for extending its capabilities:

«The results of our paper allow modifying the Panka et al. method to extend its capabilities. The simplest development of this method seems to be the following. First of all, note that the HO₂ equilibrium condition (9) depends on H and O only and can be used within the self-consistent retrieval procedure, considering the following system of equations:

$$OH(v = 1 - 9) = \frac{k_{12} \cdot H \cdot O_3 \cdot M \cdot f(v) + \sum_{v' > v} (a_1(v', v) + a_2(v', v) \cdot O_2 + a_3(v', v) \cdot N_2 + (a_4(v', v) + a_5(v', v)) \cdot O) \cdot OH(v')}{a_6(v) \cdot O + \sum_{v' > v} (a_1(v, v') + a_2(v, v') \cdot O_2 + a_3(v, v') \cdot N_2 + (a_4(v, v') + a_5(v, v')) \cdot O)},$$

$$OH(0) = \frac{\sum_{v' > 0} (a_1(v', 0) + a_2(v', 0) \cdot O_2 + a_3(v', 0) \cdot N_2 + (a_4(v', 0) + a_5(v', 0)) \cdot O) \cdot OH(v') + k_{18} \cdot O \cdot HO_2 + 2 \cdot k_{14} \cdot H \cdot HO_2}{k_{17} \cdot O},$$

$$HO_2 = \frac{k_{20} \cdot H \cdot M \cdot O_2}{k_{18} \cdot O + (k_{14} + k_{15} + k_{16}) \cdot H},$$

$$VER_{2\mu m} = a_1(9, 7) \cdot OH(9) + a_1(8, 9) \cdot OH(8),$$

$$VER_{1.6\mu m} = a_1(5, 3) \cdot OH(5) + a_1(4, 2) \cdot OH(4),$$

where a_{1-6} are the constant rates of the processes $OH(v) \rightarrow OH(v' < v) + hv$, $OH(v) + O_2 \rightarrow OH(v < v') + O_2$, $OH(v) + N_2 \rightarrow OH(v < v') + N_2$, $OH(v) + O(^3P) \rightarrow OH(v' \leq v - 5) + O(^1D)$, $OH(v) + O(^3P) \rightarrow OH(v' < v) + O(^3P)$, and $OH(v) + O(^3P) \rightarrow H + O_2$, respectively. Note this system includes 13 equations with 13 unknown variables. Therefore, the solution to the system for a set of the SABER data (simultaneously measured profiles of O₃, T, pressure, $VER_{2\mu m}$, and $VER_{1.6\mu m}$) gives one simultaneously retrieved profiles of O, H, OH($v=0-9$), and HO₂. By applying the criteria (17) and (25) to obtained O and H profiles, we verify the fulfillment of OH and HO₂ equilibrium conditions and determine the height below which the resulting profiles should be cut. More advanced retrieval procedure would be statistical, based on Bayesian theorem, taking into account the uncertainties in measurement data and rate constants. Similar, for example, to Kulikov et al. (2018a), it should include a derivation of posterior conditional probability density function of retrieved characteristics and numerical analysis of this function. Detailed development of this retrieval method is outside of this paper and should be carried out in a separate work.»

* This manuscript is for a technical note. The number of figures seems rather excessive (11 figures with 155 panels). The text does a good job describing the main point of the figures. It would seem practical to include most figures in a supplementary section.

Following this remark and the remark by the Referee 3, we organized the Supplement. In the revised manuscript, the Figures 3-8 were reduced to Figures 3-4. The complete figures for major reactions with all 12 panels for each month are presented in Supplement. Figure 12 was deleted. As

a result, the number of Figures was reduced from 12 to 8, and the total number of panels on them was reduced from 143 to 75.

* Author Contributions: Co-authorship for the last three authors who “contributed to reviewing the article” seems somewhat unusual. Also, please note that the last initials should be AF and not AM (Line 434).

In the revised manuscript, Author Contributions was corrected as following:

«Conceptualization: MK, MB, AC, SD, AF. Methodology: MK, AF. Investigation: MK, MB, AC, SD. Software: MB, AC. Visualization: MB, AC. Funding Acquisition: MK. Writing – original draft preparation: MK, MB. Writing – review & editing: AC, SD. Supervising: AM.»

Technical Corrections

Line 19: ...conditions describe the... ...the top to some lower borders...

Line 21: ...criteria reproduce well...

Line 22: ...allow to extend previously proposed...

Line 35: ...components: in particular, trace gases with short lifetimes relative to...

Line 47: ...approximation has been used...

Line 79: ...this approximation's validity

Line 80: ...there is no assessment of...

Line 85: ...maps of the components of interest.

Line 92: ...apply this approach to the analysis...

Line 100: ...all excited and ground states...

Line 128: ...To remove the transition regions...

Line 146: ...Finally, we obtained...

Line 147: ...the poorly chemical evolution...???

Line 152: ...from the total sink of n.

Line 169: ...Figure 1 plots...

Line 173: ...see the presence of...

Line 206: ...Figure 3 shows...

Line 215: ...Figure 4 presents...

Line 231: ...up to a 95% contribution to the equilibrium concentration.

Line 243: ...major in the lower part of...

Line 256: ...are different from those...

Line 261: ...As a result, the...

Lines 263: The punctuation (comma, in this case) appears to be incorporated in the equation. Similar comment for other equations. A few equations do not have punctuation. This issue could be resolved at the copy-editing stage.

Line 265: Figure 9 shows ...

Line 271: ...reproduces many features of...

Line 276: Figure 10 plots...

Line 288: Criteria for HO₂ and...

Line 290: Let us determine...

Line 295: Let us find...

Line 297: "analyzed analytically" ???

Line 300: ...rewritten in the following...

Line 316: "first of all" seems redundant

Line 317: ...As previously mentioned, near and above the OH...

Line 331: There is a formatting problem with the equation.

Line 335: There is a formatting problem with the equation.

Line 339: ...the red line...

Line 347: We will now discuss the obtained results...

Line 348: As noted, Figs. 9-10...

Line 349: Recently, Kulikov et al. (2023) found such a feature...

Line 355: "At middle," ???

Line 360: "From simplified Eqs. (17) and (25), it follows that..."

Line 370: As a result,...

Line 372: There is a formatting problem with the equation.

Line 376: ...including this additional term...

Line 378: As noted in the Introduction...

Line 379: ...constitute a useful tool for retrieval of these components...

Line 384: ...including improvement of existing retrieval...

Line 387: ...valid for excited states...

Line 389: ...lifetime is determined by the reaction...

Line 398: ...the constant rates...

Line 406: ...in accordance with... OR ...according to...???

Line 439: Is the Acknowledgements section missing or is it the same as Financial Support?

Line 442: ...and State assignment No. 0729...

Line 469: ...a model study...

Line 511: SABER data...

Line 638: ...averaged relative contribution...

Line 642: ...averaged relative contribution...

Line 646: ...averaged relative contribution...

Line 650: ...averaged relative contribution...

Line 654: ...averaged relative contribution...

Line 659: ...averaged relative contribution...

All Referee's remarks were taken into account, the manuscript was corrected accordingly. Moreover, the final revised manuscript will be verified and corrected by a professional translator.

Other changes are related to the recommendations of other referees.

Thank you for taking your time to review our manuscript.

With respect,

Michael Kulikov, Michael Belikovich, Alexey Chubarov, Svetlana Dementyeva, and Alexander Feigin