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 2

Major comment

The approach describes, evaluates, and compares several expressions to determine equilibrium. The standard for evaluation is how well a particular equilibrium value computed from their 3-D chemical transport model agrees with the actual concentrations simulated in the same model. Winds used for transport and temperatures for chemical rate coefficients are based on temporal smoothing of once-daily values from a middle atmosphere dynamics model. My concern is that this approach excludes the transport and large temperature swings associated with tides. In the tropical MLT, vertical winds associated with the migrating diurnal tide can be quite substantial and are a leading transport process. Temperature variations of 10-20 K in a few hours are seen during some seasons. As a result of this omission, the actual variations of species concentrations that go into the analyses may be more variable than those simulated, which would affect the standard deviation criteria in Eq. (1). This omission may have led to a diagnosis of equilibrium that is more optimistic than the reality for the equatorial region.

It seems to me that the only way to quantify the importance of tides would be to perform a simulation with input dynamical fields taken more frequently. Without this, it is necessary to add some sentences that point out this omission and its possible implications for the results.

During the revision period, we carried out additional modelling with 3D distributions of the main characteristics taken from the Canadian Middle Atmosphere Model (CMAM) for the year 2009 (Scinocca et al., 2008) updated with the 6 hour of frequency. CMAM is known to reproduce tides e.g. McLandress, 1997; Jonsson et al., 2002). The analysis of the height-time evolution of OH and HO₂, especially in the tropical latitudes, showed that our criteria well reproduce the changes of the OH and HO₂ equilibrium boundaries in such conditions (see Figure below).


\[ \frac{\text{HO}_2}{\text{HO}_2^\text{eq}} \quad \text{(two top panels) and } \frac{\text{OH}}{\text{OH}^\text{eq}} \text{ (two bottom panels) time-height variations above the Equator (2.8°S,0°W) in March and June 2009 calculated with the use of the temperature and winds distributions from the Canadian Middle Atmosphere Model. The stippling shows daytime. The white area represents the } \frac{\text{HO}_2}{\text{HO}_2^\text{eq}} \text{ and } \frac{\text{OH}}{\text{OH}^\text{eq}} \text{ ratios outside the [0.5, 1.5] interval. Magenta lines point the borders of } \text{HO}_2 \text{ and OH equilibrium according to criteria (17) and (25) (} \text{Crit}_{\text{HO}_2} = 0.1 \text{ and } \text{Crit}_{\text{OH}} = 0.1).} \]
This Figure can be found in the Supplement (Figure S27). In the Discussion of the revised manuscript, we have added the following paragraph to address the issue:
«The main results were obtained using a 3D model with temperature and wind distributions updated every 24 hours. This excluded the influence of the atmospheric wave motion, in particular, associated with tides, which is one of the main dynamical drivers in the tropical mesopause. We carried out additional modeling with the distributions of the main characteristics computed by the Canadian Middle Atmosphere Model for the year 2009 (Scinocca et al., 2008) with a 6-hourly frequency for updating. The analysis of the time-height evolution of OH and HO₂, especially, at low latitudes showed that our criteria well reproduce the local variations of the OH and HO₂ equilibrium boundaries in such conditions.»

Other comments
(Figure captions) In some cases, the captions and text do not explain the figures sufficiently. In particular, the captions to Figures 1 and 9 are almost identical; the exception being a subscript “sh” in one of the terms in the Figure 9 caption. The situation for Figures 2 and 10 is similar. Please add words giving more information so the differences are more obvious.

In the revised manuscript, these Figure captions were corrected accordingly:
«Figure 1. Nighttime mean and monthly averaged $\text{HO}_2/\text{HO}_2^{eq}$, where $\text{HO}_2^{eq}$ is equilibrium concentration determined by Eq. (4). Black line shows the border of HO₂ equilibrium according to condition (1). The stippling corresponds to $\chi<105^\circ$. The white area represents the $<\text{HO}_2/\text{HO}_2^{eq}>$ ratio outside the $[0.5, 1.5]$ interval.

Figure 2. Nighttime mean and monthly averaged $\text{OH}/\text{OH}^{eq}$, where $\text{OH}^{eq}$ is equilibrium concentration determined by Eq. (5). Black line shows the border of OH equilibrium according to condition (1). The stippling corresponds to $\chi<105^\circ$. The white area represents the $<\text{OH}/\text{OH}^{eq}>$ ratio outside the $[0.5, 1.5]$ interval.

Figure 5. Nighttime mean and monthly averaged $\text{HO}_2/\text{HO}_2^{eq}_{sh}$, where $\text{HO}_2^{eq}_{sh}$ is shortened equilibrium concentration determined by Eq. (9). Black line shows the border of HO₂ equilibrium according to condition (1). Magenta line shows $<\text{Crit}_{\text{HO}_2}> = 0.1$. The stippling corresponds to $\chi<105^\circ$. The white area represents the $<\text{HO}_2/\text{HO}_2^{eq}>$ ratio outside the $[0.5, 1.5]$ interval.

Figure 6. Nighttime mean and monthly averaged $\text{OH}/\text{OH}^{eq}_{sh}$, where $\text{OH}^{eq}_{sh}$ is shortened equilibrium concentration determined by Eq. (10). Black line shows the border of OH equilibrium according to condition (1). Magenta line shows $<\text{Crit}_{\text{OH}}>= 0.1$. The stippling corresponds to $\chi<105^\circ$. The white area represents the $<\text{OH}/\text{OH}^{eq}>$ ratio outside the $[0.5, 1.5]$ interval.»
Can you provide references or more detail to support the idea that limited measurements of trace species can be used to retrieve temperature, reaction rates, chemical sources, etc? This comes across as wishful thinking that might not hold up because of multiple uncertainties in the components of the photochemical system.

In the revised manuscript, this sentence has been corrected as follows:

«These relationships can be used to derive information about hard-to-measure atmospheric species, determine key atmospheric characteristics (for example, temperature (Marchand et al., 2007)), validate the data quality of simultaneous measurements of several atmospheric components (Kulikov et al., 2018a), estimate reaction rate constants (Stedman et al., 1975; Avallone and Toohey, 2001), evaluate sources/sinks (Cantrell et al., 2003), etc.»


The two sentences (beginning “Secondly, there is no detailed numerical evaluation ..”) are confusing. This paragraph is about night ozone, which you examined in earlier papers. Have you switched the discussion to HOx without informing the reader or are you raising doubts about your 2019 and 2023 papers on ozone equilibrium?

In the revised manuscript, these sentences have been replaced as follows:

«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.»

(line 101) “this approach is tested” It seems that you test the equilibrium timescale for ground-state OH but not for the vibrationally excited states that are important components in the model of Panka et al. Please revise to make this distinction clear.

In the revised manuscript, this paragraph has been corrected as follows:

«In particular, Panka et al. (2021) proposed the method for nighttime total OH retrieval from SABER/TIMED data at 80-100 km, which does not use the ozone chemical equilibrium. However, the method applies the equilibrium between sources and sinks not only for excited states of OH with ultrashort lifetimes, but also for the ground state. Therefore, this point is verified in our paper.»

(Section 6) It was difficult to get oriented toward this analysis. Please add a sentence or more at the beginning of the section referring the reader to Eq (2) and also please reiterate the key takeaway from the discussion describing the difference between the terms “lifetime” and “local time scale”. Other readers may, like me, be unfamiliar with the distinction between these concepts and their role in your analysis.

In the revised manuscript, the Section 2 «Used 3D model and Approaches» has been extended to address this remark:

«Finally, we obtained and verified the analytical criteria of OH and HO₂ nighttime chemical equilibria according to Kulikov et al. (2023a). The paper considered the pure chemical evolution of a certain trace gas \( n \):

\[
\frac{dn}{dt} = I_n - S_n = -\frac{1}{\tau_n} (n - n^{eq}),
\]

\[
\tau_n = \frac{n}{I_n}, \quad n^{eq} = \frac{n I_n}{S_n}, \quad (2)
\]

where \( t \) is time, \( I_n \) and \( S_n \) are total photochemical/chemical sources and sinks of \( n \), respectively, \( \tau_n \) is the \( n \) lifetime, and \( n^{eq} \) is its equilibrium concentration corresponding to the condition \( I_n = S_n \). The lifetime determines the characteristic time scale for which \( n \) approaches \( n^{eq} \), when \( n^{eq} = const \). In general case, \( \tau_n \) and \( n^{eq} \) are functions of time. Kulikov et al. (2023a) showed strictly mathematically that the local values of \( n \) and \( n^{eq} \) are close to each other \( (n(t) \approx n^{eq}(t)) \), when \( \tau_n \ll \tau_{n^{eq}} \), where \( \tau_{n^{eq}} \) is the local time scale of \( n^{eq} \):

\[
\tau_{n^{eq}} \equiv \frac{n^{eq}}{|dn^{eq}/dt|}, \quad (3)
\]
The expression for $\tau_n$ is found from the total sink of $n$. The expression for $\tau_{n_{eq}}$ is derived from Eq. (3) with the use of differential equations describing chemical evolution of other reacting components, which determine the expression for $n_{eq}$. Kulikov et al. (2023a) also showed, when $\tau_n \ll \tau_{n_{eq}}$, $n \approx n_{eq}(1 - \text{sign}\left(\frac{dn_{eq}}{dt}\right) \cdot \frac{\tau_n}{\tau_{n_{eq}}})$ in the first order approximation. Thus, the criterion

$$\frac{\tau_n}{\tau_{n_{eq}}} \leq 0.1$$

(4)

is sufficient, in order to the possible difference between $n$ and $n_{eq}$ to be no more than 0.1.

Is the analysis of ozone equilibrium in Section 7 (lines 348-362) relevant to the present paper? If so, please explain the connection. If this paragraph remains, please provide some transition words to let the reader know when you are switching your focus from ozone to HOx.

In the revised manuscript, this paragraph has been corrected as follows:

«As noted, Figs. 5-6 present an interesting peculiarity. At the middle latitudes, summer $z_{HO_2}^{eq}_{sh}$ and $z_{OH}^{eq}_{sh}$ are remarkably higher than winter ones. Recently, Kulikov et al. (2023b) found such a feature in the evolution of nighttime ozone chemical equilibrium boundary derived from SABER/TIMED data, which was accompanied by the same variation of the transition zone separating deep and weak photochemical oscillations of O and H caused by the diurnal variations of solar radiation. The authors analyzed this effect near and below the transition zone. It was shown, first, that nighttime O decreases with the characteristic time scale $\tau_O = O/|dO/dt|$ proportional to the $O/H$ ratio at the beginning of the night. Second, during the summer, the daytime $O/H$ at the middle latitudes is remarkably less than the one in winter. Consequently, summer values of $\tau_O$ are significantly shorter than winter ones, so summer O during the night decreases much faster than in winter. In our case, lifetimes of HO$_2$ and OH are proportional mainly to $\frac{1}{O}$ (see Eqs. (11) and (19)), so the summer rise of $z_{HO_2}^{eq}_{sh}$ and $z_{OH}^{eq}_{sh}$ can be explained by the season difference in O diurnal evolution at these latitudes.»

(line 391) “one can see from Figure 8” Should this be Figure 7 or Figures 7 and 8?

In the revised manuscript, it should be Figure 6. Corrected.

Editorial comments
Throughout: I’m not sure of the journal’s style guidelines but, for me as a reader, it would be really helpful if you indicated that something is an equation when the number appears in the text. For example (line 141), replace “from 1” with “from Eq. (1)” or something similar.
(line 51) “of a critical parameters” -> “of critical parameters”
(line 66) Sentence beginning “First …” is not clear. Is this what you mean? “First, there are no clear criteria indicating the conditions under which the equilibrium conditions are satisfied?”
(line 71) “is too short varying” -> “varies”
(line 83) “to correct search of” -> “to correctly search for”
(line 100) “exited” -> “excited”
(line 128) “we took into account the local time” -> “we use only local times”
(line 147) “the poorly chemical evolution” It is not clear what this means.
(line 170) “dashed area” -> “stippling” Also this sentence would fit better in the figure caption than the main text.
(line 173) “present” -> “presence”
(line 263) apostrophe in denominator
(line 288) “criterions” -> “criteria”
(line 290, 295) “Let” is an awkward word here. How about replace the first instance (line 290) with “First, we” and the second (line 295) with “Then”
(line 310, 343) “in zero approximation” do you mean “in the zeroth order approximation”? 
(line 351) “whichwas” -> “which was”
(line 352-355) This sentence is too long and convoluted and the point being made is not clear. What are “nighttime evolution times”? In the next sentence, what does “At middle” refer to?
(line 360) “It is follows” -> “It follows”
(line 426) “is going to retrieve” Do you mean “allows the retrieval of”?

All Referee remarks have been taken into account and the manuscript has been 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