Technical Note: Nighttime OH and HO_2 chemical equilibria in the mesosphere – lower thermosphere

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Abstract. At the altitudes of the mesosphere – lower thermosphere~~,~~ OH and HO_2 play a significant role in many physicochemical processes. Thus, monitoring ~~of~~ their spatiotemporal evolution together with other chemically active trace gases is one of the most important problems for this atmosphere region, in which direct measurements are difficult. The paper studies the nighttime OH and HO_2 chemical equilibria using the 3D chemical transport modeling within the general approach ~~including~~, which includes the ~~extraction~~identification of the main sources and sinks in the equilibrium space-time areas and derivation of analytical criteria for equilibrium validity. The presented analysis shows, that there are extended areas, where nighttime HO_2 and OH are close to their local equilibrium concentrations, determined mainly by the reaction between HO_x – O_x components among themselves and with H_2O_2, N, NO, NO_2~~,~~ and CO. In the upper mesosphere – lower thermosphere~~,~~ the equilibrium expressions can be shortened, ~~including~~so that they include the HO_x – O_x chemistry only. These ~~conditions describes~~expressions describe the HO_2 and OH ~~equilibrium~~equilibria from the top down to ~~the~~ some ~~lower borders~~boundaries, the altitude ~~position~~positions of which vary in the interval between 72-73 and 85 km and ~~depends~~depend essentially on season and latitude. The developed analytical criteria almost everywhere ~~well~~ reproduce well the main features of these ~~borders.~~boundaries. Due to weak sensitivity to uncertainties of reaction rates and other parameters, the criteria can be considered a robust instrument for HO_2 and OH equilibrium validation. The obtained results allow us to extend ~~the abilities of~~ previously proposed methods for the retrieval of poorly measured components from measurement data and to develop new approaches.

1 Introduction

Monitoring the spatiotemporal evolution of chemically active trace gases is one of the most important problems in atmospheric research. Despite the increase of the experimental data volume nowadays, primarily due to the development ~~of~~in remote sensing methods, many important trace gases continue to be unavailable for direct and regular measurements. A well-known way to increase the information content of experimental campaigns is to use ~~chemical transport models and~~the available experimental data ~~for deriving~~in conjunction with a certain chemical or physicochemical model to derive unmeasured characteristics indirectly. Within the framework of this approach, the model acts as *a priori* relationship between directly measured and retrieved characteristics. The simplest model, that makes it possible to implement this approach, is based on the condition of local (in both time and space) photochemical/chemical balance (local equilibrium) between sources and sinks of the so-called "fast" components: trace gases with short lifetimes relatively, in particular, to the characteristic transport times. Mathematically~~,~~ this condition does not mean that the fast variables are at equilibrium, but when it is fulfilled, the corresponding concentrations are close to their instantaneous equilibrium values. At the same time~~,~~ due to the strong dissipation~~,~~ in most cases (except the special cases where the ensemble of fast components includes the slow family of these components), there is no need to follow the law of matter conservation. It is possible to ~~discard~~disregard insignificant sinks and sources, including those caused by transport, in the corresponding balance equations without the loss of accuracy~~, including those caused by transport~~. The resulting algebraic equations are the simplest *a priori* local relations between measurable and retrieved trace gases. 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 ~~known with high uncertainty,~~(Stedman et al., 1975; Avallone and Toohey, 2001), evaluate sources ~~(emissions~~/sinks (Cantrell et al., 2003), etc.

For several decades~~,~~ the photochemical/chemical equilibrium approximation ~~have~~has been used to solve many atmospheric tasks. It is applied (see, e.g., the short review in Kulikov et al. (2018a) and references therein) in investigations of the surface layer and free troposphere chemistry in different regions (over ~~megalopolises~~megapolises, in rural areas, in the mountains, over the seas), in stratospheric chemistry studies, including derivation of ~~a~~ critical parameters ~~of~~in the ozone destruction catalytic cycles, and ~~to study~~in studies of the HO_x – O_x chemistry and airglows **(**$O(^1S)$ green-line, O_2 A-band, OH Meinel band emissions**)** at the heights of the mesosphere – lower thermosphere. In the latter case~~,~~ the distributions of unmeasured characteristics are determined from the data of daytime and nighttime rocket and satellite measurements (e.g., Evans and Llewellyn, 1973; Good, 1976; Pendleton et al., 1983;

McDade et al., 1985; McDade and Llewellyn, 1988; Evans et al., 1988; Thomas, 1990; Llewellyn et al., 1993; Llewellyn and McDade, 1996; Russell and Lowe, 2003; Russell et al., 2005; Kulikov et al., 2006, 2009, 2017, 2022a, 2022b; Mlynczak et al., 2007, 2013a, 2013b, 2014, 2018; Smith et al., 2010; Xu et al., 2012; Siskind et al., 2008, 2015; Fytterer et al., 2019) with the use of equilibrium assumptions for ozone and excited states of OH, O, and O_2. For example, such an approach is applied to the data of the SABER (Sounding of the Atmosphere using Broadband Emission Radiometry) instrument onboard the TIMED (Thermosphere Ionosphere Mesosphere Energetics and Dynamics) satellite, which since 2002 continues to measure simultaneous profiles of temperature, ozone~~,~~ and volume emission rates of OH* transitions in wide ranges of altitude, local time~~,~~ and latitude with a rather high space-time resolution.

Note a number of general aspects of the application of equilibrium conditions in the above examples. First of all, there are no clear criteria ~~why~~, indicating the conditions under which the use of equilibrium ~~condition should be satisfied.~~approximation is justified. Usually~~,~~ a certain component is taken to be a fast variable, if its lifetime is much shorter, than the lifetimes of other components of studied photochemical/chemical system or the duration of a day, daytime, nighttime, etc. For example, in the papers on SABER data processing (Mlynczak et al., 2013a, 2013b, 2014, 2018~~),~~) it is assumed, that the nighttime ozone chemical equilibrium in the mesopause is well fulfilled at altitudes of 80–100 km, since the nighttime ozone lifetime at these altitudes ~~is too short varying~~varies in the range from several minutes to several tens of minutes. Note, that this assumption is quite popular and used in different tasks (e.g., Swenson and Gardner, 1998; Marsh et al., 2006; Smith et al., 2009; Nikoukar et al., 2007; Xu et al., 2010, 2012; Kowalewski et al., 2014; Grygalashvyly et al., 2014; Grygalashvyly, 2015; Sonnemann et al., 2015; Kulikov et al., 2021). Belikovich et al. (2018) and Kulikov et al. (2018b, 2019, 2023a) analyzed the nighttime ozone chemical equilibrium numerically, analytically, and with the use of SABER/TIMED data. It was revealed, that the short lifetime is not a sufficient condition, so, this equilibrium may be significantly ~~disrupted~~disturbed above 80 km. ~~Secondly, there is no detailed numerical examination of this approximation validity, depending on altitude, latitude,~~ The local ~~time,~~ratio between true and ~~season. Correspondingly, there is no~~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 ~~assessment of possible errors~~error in retrieved characteristics due to ~~disturbance of the used equilibrium condition~~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.

~~Starting since our~~ Since the papers ~~by~~of Belikovich et al. (2018) and Kulikov et al. (2018b, 2019, 2023a), we ~~develop~~developed the general approach to ~~correct search of~~correctly identify fast components ~~using~~, employing the data from a global 3D chemical transport model. It includes:

1. Plotting of the equilibrium space-time maps of ~~interested component.~~the components of interest.

2. Identification of the main sources and sinks in the found equilibrium areas.

3. Derivation and subsequent use of analytical criteria that make it possible to determine the fulfillment of the equilibrium condition locally (in time and space) with the use of the measurement data only.

The ~~last~~latter point is based on the theory of chemical equilibrium of a certain trace gas ~~based on~~, acquired from estimations of its lifetime and equilibrium concentration, and time dependences of these characteristics (Kulikov et al., 2023a). Note, that 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.

The main ~~goals~~goal of ~~this~~the paper is to apply ~~mentioned~~this approach ~~for~~to the analysis of nighttime OH and HO_2 chemical ~~equilibriums~~equilibria in the mesosphere – lower thermosphere. Along with O and H, OH and HO_2 are important components of HO_x – O_x chemistry, participating (a) in chemical heating through, in particular, $O+OH \rightarrow O_2+H$ and $O+HO_2 \rightarrow O_2+OH$ exothermic reactions, (b) in formation of airglows, (c) in catalytic cycles of the ozone destruction. Moreover, the equilibrium conditions of OH and HO_2 are additional *a priori* relationships, that can be used to retrieve these components or other characteristics from measured data. In particular, ~~the method proposed by~~ 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 ~~nighttime~~ ozone chemical equilibrium~~, but nevertheless,~~. However, the method applies the equilibrium between sources and sinks ~~for all exited and ground~~ not only to excited states of OH ~~(v=0-9).~~with ultrashort lifetimes, but also to the ground state. Therefore, this ~~approach~~point is ~~tested~~verified in our paper.

In the next section~~,~~ we present the used model and methods. In Section 3~~,~~ the model data are used to plot HO_2 and OH equilibrium maps. In Sections 4-5~~,~~ we ~~extract~~identify the main reactions, determining equilibria of these gases, and present their shortened equilibria conditions at the upper mesosphere and lower thermosphere altitudes. In Section 6~~,~~ the criteria for HO_2 and OH equilibria validity are developed. In Section 7~~,~~ we discuss the obtained results and their possible applications.

2 Used 3D model and Approaches

The analysis of OH and HO_2 nighttime chemical equilibria was carried out, using the data, obtained with calculation of 3D chemical transport model of the middle atmosphere, developed at the Leibniz Institute of Atmospheric Physics (e.g., Sonnemann et al., 1998; Körner & Sonnemann, 2001; Grygalashvyly et al., 2009; Hartogh et al., 2004, 2011) to investigate the mesosphere – lower thermosphere chemistry, in particular, in the extended mesopause region. A number of papers (e.g.,

Hartogh et al., 2004, 2011; Sonnemann, et al., 2006, 2008) validated the model with measurements, in particular, for ozone and water ~~vapour~~vapor.

The space-time distribution of temperature and winds were taken from the model of the dynamics of the middle atmosphere COMMA-IAP (e.g., Kremp et al., 1999; Berger and von Zahn, 1999) with an updated frequency of 1 day and linear smoothing between subsequent updates to avoid unrealistic jumps in the calculated concentrations of trace gases. 3D advective transport is taken into account with the use of the Walcek-scheme (Walcek, 2000). The vertical diffusive transport (turbulent and molecular) is calculated with the use of the implicit Thomas algorithm (Morton and Mayers, 1994). The model grid ~~includes~~has 118 pressure-~~head~~height levels (0–135 km), 16 latitudinal and 32 longitudinal levels. The chemical module (see Table 1) comprises 25 constituents (O, $O(^1D)$, O_3, H, OH, HO_2, H_2O_2, H_2O, H_2, N, NO, NO_2, NO_3, N_2O, CH_4, CH_2, CH_3, CH_3O_2, CH_3O, CH_2O, CHO, CO, CO_2, O_2, N_2), 54 chemical reactions between them~~,~~ and 15 photo-dissociation reactions. The model utilizes the pre-calculated dissociation rates (Kremp et al., 1999) and their dependence on the altitude and solar zenith angle.

The model was used to calculate a one-year global evolution of the above mentioned trace gases. ~~For removing~~To remove the transition regions corresponding to sunset and sunrise, we ~~took into account the~~use only local ~~time~~times when the solar zenith angle ~~> 95~~$\chi > 105°$. As a result, we find the spatiotemporal series of the OH/OH^{eq} and $HO_2/{HO_2}^{eq}$ ratios. Here~~,~~ OH and HO_2 are the local nighttime values of hydroxyl and ~~hydroperoxy~~hydroperoxyl radicals, calculated by the model, OH^{eq} and ${HO_2}^{eq}$ are their local equilibrium values, corresponding to the instantaneous balance between production and loss terms~~,~~ respectively. ~~Therefore, for determination of~~ To determine each local value of OH^{eq} and ${HO_2}^{eq}$~~,~~ we used the local values of the parameters (temperature, O_2, and N_2) and the concentrations of other trace gases, determining local chemical sources and sinks of OH and HO_2. Then~~,~~ the OH/OH^{eq} and $HO_2/{HO_2}^{eq}$ series were averaged over the zonal coordinate and time during each month and were presented as height-latitude maps, depending on the month. Each map contains lines, marking the boundaries of the equilibrium areas, where the following conditions are satisfied:

$$\begin{cases} |< OH/OH^{eq} > -1| \le 0.1 \\ \sigma_{OH/OH^{eq}} \le 0.1 \end{cases}, \begin{cases} |< HO_2/{HO_2}^{eq} > -1| \le 0.1 \\ \sigma_{HO_2/{HO_2}^{eq}} \le 0.1 \end{cases}, \quad (1)$$

where the angle brackets are used to denote the values averaged in time and space, $\sigma_{OH/OH^{eq}}$ and $\sigma_{HO_2/{HO_2}^{eq}}$ are standard deviations of the OH/OH^{eq} and $HO_2/{HO_2}^{eq}$ ratios from 1~~,~~ respectively.

Then~~,~~ we plotted spatiotemporal maps, showing the relative contribution of each reaction to a summarized source or sink at all altitudes and latitudes. These maps helped us to identify the main sources and sinks, describing the chemical equilibrium of nighttime OH and HO_2 in the equilibrium areas to an accuracy of better than a few percent.

~~At final stage~~Finally, we obtained and verified the analytical criteria of OH and HO_2 nighttime chemical equilibria according to Kulikov et al. (2023a). The paper considered the ~~poorly~~pure chemical evolution of a certain trace gas n~~. It was shown~~:

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

$$\tau_n = \frac{n}{S_n}, \; n^{eq} = \frac{n \cdot I_n}{S_n}, \quad (2)$$

where t is time, I_n and S_n are total photochemical/chemical sources and sinks of n respectively, τ_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 τ_n and n^{eq} are functions of time. Kulikov et al. (2023a) showed strictly mathematically, that the local values of n and ~~its equilibrium concentration~~ n^{eq} are close to each other ($n(t) \approx n^{eq}(t)$), when $\tau_n \ll \tau_{n^{eq}}$, where ~~τ_n is the n lifetime and~~ $\tau_{n^{eq}}$ is the local time scale of n^{eq}:

$$\tau_{n^{eq}} \equiv \frac{n^{eq}}{|dn^{eq}/dt|}.$$

~~(2~~

$$\frac{n^{eq}}{|dn^{eq}/dt|}. \quad (3)$$

The expression for τ_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 $\tau_n \ll \tau_{n^{eq}}$, $n \cong n^{eq}(1 - sign(\frac{dn^{eq}}{dt}) \cdot \frac{\tau_n}{\tau_{n^{eq}}})$ in the first order approximation. Thus, the criterion

$$\tau_n/\tau_{n^{eq}} \leq 0.1 \quad (~~3~~4)$$

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

3 Nighttime HO_2 and OH chemical ~~equilibriums~~equilibria

According to the Table 1~~,~~ HO_2 chemical sources in nighttime are determined by the following reactions:

H+O_2+M → HO_2+M (R20), OH+O_3 → O_2+HO_2 (R22), H_2O_2+OH → H_2O+HO_2 (R29), H_2O_2+O → OH+HO_2 (R19), CHO+O_2 → HO_2+CO (R40), CH_3O+O_2 → CH_2O+HO_2 (R37),

whereas chemical sinks of this component are as follows:

HO_2+O → OH+O_2 (R18), HO_2+O_3 → OH+2O_2 (R23), OH+HO_2 → H_2O+O_2 (R28), H+HO_2 → 2OH (R14), H+HO_2 → H_2O+O (R15), H+HO_2 → H_2+O_2 (R16), NO+HO_2 → NO_2+OH (R50), HO_2+HO_2 → H_2O_2+O_2 (R30), HO_2+HO_2+M → H_2O_2+O_2+M (R31).

Thus, HO_2 local equilibrium concentration is described by the following equation:

$$HO_2^{eq} = \frac{k_{20}\cdot H\cdot M\cdot O_2+k_{22}\cdot OH\cdot O_3+k_{29}\cdot H_2O_2\cdot OH+k_{19}\cdot H_2O_2\cdot O+k_{40}\cdot CHO\cdot O_2+k_{37}\cdot CH_3O\cdot O_2}{k_{18}\cdot O+k_{23}\cdot O_3+k_{28}\cdot OH+(k_{14}+k_{15}+k_{16})\cdot H+k_{50}\cdot NO+2\cdot(k_{30}+k_{31}\cdot M)\cdot HO_2} \quad (45)$$

The Figure 1 plots height-latitude cross sections for the $< HO_2/HO_2^{eq} >$ ratio for each month. The dashed area corresponds to χ<95°. The white area represents the ratio outside the [0.5, 1.5] interval. The black solid lines mark the bordersboundaries of equilibrium areas, where, according to condition (1),) local values of HO_2 are close to their equilibrium values with a possible bias of less than 10%. At low and middle latitudes, one can see the presentpresence of the main equilibrium area, which extends from the top of the analyzed altitude range to the lower boundary. The height of this equilibrium borderboundary, $z_{HO_2^{eq}}$, depends on the season and latitude and varies in the interval between 73 and 85 km. It is the highest and the lowest during the summer and winter respectively at the middle latitudes. Near the equator, $z_{HO_2^{eq}}$ demonstrates the weakest annual variations and varies in the range of 81-83 km range. There are local areas below the upper longest black line, but they are small and irregular and can be omitted from our consideration. Note only that the maps in many months show the existence of equilibrium near 50 km, which can be assumed to be the beginning of the main equilibrium area in the stratosphere. At high latitudes, there is the main equilibrium area as at low and middle latitudes, but this area above 70-75° of latitude can extend down to 50 km with small exceptions.

In accordance to the Table 1, OH chemical sources are determined by the following reactions:

H+O_3 → OH+O_2 (R21), HO_2+O → OH+O_2 (R18), HO_2+O_3 → OH+2O_2 (R23), H+HO_2 → 2OH (R14),

NO+HO_2 → NO_2+OH (R50), H_2O_2+O → OH+HO_2 (R19), H +NO_2 → OH+NO (R51), O(^{1}D)+H_2O → 2OH (R7), O(^{1}D)+H_2 → H+OH (R8), CH_4+O(^{1}D) → CH_3+OH (R9),

whereas chemical sinks of this component are as follows:

OH+O → H+O_2 (R17), OH+O_3 → O_2+HO_2 (R22), OH+HO_2 → H_2O+O_2 (R28), OH+OH → H_2O+O (R26), OH+OH+M → H_2O_2+M (R27), H+OH+N_2 → H_2O+N_2 (R24), H_2O_2+OH → H_2O+HO_2 (R29), OH+CO → H+CO_2 (R32), CH_4+OH → CH_3+H_2O (R33), OH+H_2 → H_2O+H (R25), N+OH → NO+H (R49).

Thus, OH local equilibrium concentration is described by the following equation:

$$OH^{eq} = (k_{21} \cdot H \cdot O_3 + k_{18} \cdot O \cdot HO_2 + k_{23} \cdot HO_2 \cdot O_3 + 2 \cdot k_{14} \cdot H \cdot HO_2 + k_{50} \cdot HO_2 \cdot NO + k_{19} \cdot H_2O_2 \cdot O + k_{24} \cdot H \cdot N_2 + k_{51} \cdot NO_2 \cdot H + 2 \cdot k_7 \cdot O(^1D) \cdot H_2O + k_8 \cdot O(^1D) \cdot H_2 + k_9 \cdot O(^1D) \cdot CH_4) / (k_{17} \cdot O + k_{22} \cdot O_3 + k_{28} \cdot HO_2 + 2 \cdot (k_{26} + k_{27} \cdot M) \cdot OH + k_{29} \cdot H_2O_2 + k_{32} \cdot CO + k_{33} \cdot CH_4 + k_{25} \cdot H_2 + k_{25} \cdot N) \quad (56)$$

Figure 2 shows height-latitude cross sections for the $< OH/OH^{eq} >$ ratio for each month. In this case, the equilibrium covers up to 70-80% of the presented ranges of heights and latitudes, so that the black solid lines mark the external bordersboundaries of non-equilibrium areas. In March and September, this area is almost symmetrical to the equator. In April-August, it is shifted towards the northern hemisphere. In October-February, this area is higher in the southern hemisphere. In all months, it is below 85-86 km. In the polar regions, there are latitudinal ranges, where OH is close to equilibrium throughout the entire range of heights.

4 The main reactions, determining HO_2 and OH equilibriumsequilibria

The Figure 3 showspresents height-latitude contour maps, showing the relative contribution of a certain reaction to the total source and sink of HO_2 in different monthsJanuary, taken forasan example. To increase the information content of the panels, the altitude range is cut off everywhere to 100 km10^{-3} hPa, since there are no significant changes above. Note, first firstly, that reaction $H+O_2+M \rightarrow HO_2+M$ determines a major (up to 95% and more) contribution in the main equilibrium area almost everywhere, except for the polar regions above 70-75° of latitude and below 75-80 km, where the reactions $OH+O_3 \rightarrow O_2+HO_2$ and $H_2O_2+OH \rightarrow H_2O+HO_2$ become important and should be taken into account. Second, other Other reactions ($H_2O_2+O \rightarrow OH+HO_2$, $CHO+O_2 \rightarrow HO_2+CO$, $CH_3O+O_2 \rightarrow CH_2O+HO_2$) together contribute less than 2-3% to the total source of HO_2 in the main equilibrium area and may be omitted.

The Figure 4 presents height-latitude contour maps showing the relative contribution of a certain reaction to the total sink of HO_2 in the same months as in Figure 3. Firstly, it should be noted thatSecondly, the reaction $HO_2+O \rightarrow OH+O_2$ determines a major (up to 95% and more) contribution to the total sink in the main equilibrium area almost everywhere, except for the same small polar areas, as in the considered case with the sources, where the reactions $HO_2+O_3 \rightarrow OH+2O_2$ and $NO+HO_2 \rightarrow NO_2+OH$ are important and should be taken into account. Secondly, theThe reactions $OH+HO_2 \rightarrow H_2O+O_2$, $H+HO_2 \rightarrow 2OH$, $H+HO_2 \rightarrow H_2O+O$, and $H+HO_2 \rightarrow H_2+O_2$ give together contribute cumulatively up to 10-15% of the total sourcesink near the boundary of the main equilibrium area. Thirdly, theThe remaining reactions ($HO_2+HO_2 \rightarrow H_2O_2+O_2$, $HO_2+HO_2+M \rightarrow H_2O_2+O_2+M$) are not important in the main equilibrium area and can be omitted.

Therefore, the expression for HO_2 local equilibrium concentration can be simplified as follows:

$$HO_2^{eq} = \frac{k_{20} \cdot H \cdot M \cdot O_2 + k_{22} \cdot OH \cdot O_3 + k_{29} \cdot H_2O_2 \cdot OH}{k_{18} \cdot O + k_{23} \cdot O_3 + k_{28} \cdot OH + (k_{14} + k_{15} + k_{16}) \cdot H + k_{50} \cdot NO} \quad (67)$$

~~Figures 5-6 show~~Figure 4 presents height-latitude contour maps, showing the relative contribution of a certain reaction to the total source and sink of OH in ~~the same months as in Figure 3~~January, taken ~~for~~as an example in Figure 3. As in the previous case, the altitude range is cut off at ~~100 km~~10^{-3} hPa, because only the panels for the reactions $H+O_3 \rightarrow OH+O_2$ and $HO_2+O \rightarrow OH+O_2$ consist of interesting variations ~~at the 100-130 km altitudes.~~above. Note, that firstly these reactions are the main OH sources in the upper part of the presented distributions down to 70-75 km, where they jointly provide up to a 95% contribution ~~in~~to the equilibrium concentration. Also~~,~~ the reaction $HO_2+O_3 \rightarrow OH+2O_2$ is major source in the lower part of the presented ~~distributions~~distribution from 50 to 60-70 km~~, depending on the month~~. The reaction $NO+HO_2 \rightarrow NO_2+OH$ is important around non-equilibrium areas of OH and should be taken into account, whereas the reaction $H+NO_2 \rightarrow OH+NO$ is important in compact altitude-latitude areas near the poles, the reaction $H+HO_2 \rightarrow 2OH$ gives up to 10-15% contribution in small areas near the equilibrium boundary. Other reactions ($O(^1D)+H_2O \rightarrow 2OH$, $O(^1D)+H_2 \rightarrow H+OH$, $CH_4+O(^1D) \rightarrow CH_3+OH$, $H_2O_2+O \rightarrow OH+HO_2$) together contribute less than 2-3% of the total source of OH in the main equilibrium area and can be omitted.

~~Figures 7-8 present height-latitude contour maps showing the relative contribution of a certain reaction to the total sink of OH. First, note that~~ Secondly, the reaction $OH+O \rightarrow H+O_2$ is the main OH sink in the upper part of the presented distributions down to 70-80 km, ~~depending on the month,~~ where it provides up to 95% of the equilibrium concentration. The reactions $OH+CO \rightarrow H+CO_2$ and $OH+O_3 \rightarrow O_2+HO_2$ are major in the ~~lover~~lower part of the presented distributions from 50 to 70-80 km~~, depending on the month.~~. The reaction $OH+HO_2 \rightarrow H_2O+O_2$ is ~~remarkable~~significant enough around non-equilibrium areas of OH, whereas the reaction $H_2O_2+OH \rightarrow H_2O+HO_2$ is important in the compact altitude-latitude area near the poles. Other reactions ($OH+OH \rightarrow H_2O+O$, $OH+H_2 \rightarrow H_2O+H$, $N+OH \rightarrow NO+H$, $CH_4+OH \rightarrow CH_3+H_2O$, $H+OH+N_2 \rightarrow H_2O+N_2$, $OH+OH+M \rightarrow H_2O_2+M$) together contribute less than 2-3% to the total ~~source~~sink of OH in the main equilibrium area and can be omitted.

Therefore, the expression for OH local equilibrium concentration can be ~~can be~~ simplified as follows:

$$OH^{eq} = \frac{k_{21} \cdot H \cdot O_3 + k_{18} \cdot O \cdot HO_2 + k_{23} \cdot HO_2 \cdot O_3 + 2 \cdot k_{14} \cdot H \cdot HO_2 + k_{24} \cdot H \cdot N_2 + k_{50} \cdot HO_2 \cdot NO + k_{51} \cdot NO_2 \cdot H}{k_{17} \cdot O + k_{22} \cdot O_3 + k_{28} \cdot HO_2 + k_{29} \cdot H_2O_2 + k_{32} \cdot CO} \quad (78)$$

5 Shortened equilibrium conditions of HO_2 and OH in the upper mesosphere and lower thermosphere

The above analysis revealed, that the reactions describing the equilibrium conditions (~~6~~ 7-8) in the lower and middle mesosphere are ~~mainly~~ different from those~~–~~ in the upper mesosphere and lower thermosphere. This means that the task of applying these conditions can be divided into two parts depending on the selected altitude range. At the upper mesosphere and lower thermosphere altitudes, we can consider only the HO_x – O_x chemistry, excluding the reactions with participation of H_2O_2, N, NO, NO_2, and CO. In addition, we can omit the reactions $HO_2+O_3 \rightarrow OH+2O_2$, $OH+O_3 \rightarrow O_2+HO_2$, and $OH+HO_2 \rightarrow H_2O+O_2$ due to their insignificance here. As ~~the~~a result, the shortened equilibrium conditions of HO_2 and OH for this altitude range are as follows:

$$HO_{2_{sh}}^{eq} = \frac{k_{20} \cdot H \cdot M \cdot O_2}{k_{18} \cdot O + (k_{14} + k_{15} + k_{16}) \cdot H}, \quad (~~8~~9)$$

$$OH_{sh}^{eq} = \frac{k_{21} \cdot H \cdot O_3 + k_{18} \cdot O \cdot HO_2 + 2 \cdot k_{14} \cdot H \cdot HO_2}{k_{17} \cdot O} \quad (~~9~~10)$$

~~The~~ Figure ~~9~~5 shows height-latitude cross sections for the $< HO_2/HO_{2_{sh}}^{eq} >$ ratio for each month. In each panel~~,~~ the upper longest black line marks the lower ~~border~~boundary of the main equilibrium area, where~~,~~ according to condition (1~~),~~) $HO_2 \approx HO_{2_{sh}}^{eq}$ with possible bias of less than 10%. As in the case of Figure 1, this area extends from the top of the analyzed altitude range. There are also very small equilibrium areas below, which can be omitted from our consideration. The height of the lower ~~border~~boundary of the main equilibrium area, ~~$z_{HO_{2_{sh}}^{eq}}$~~$z_{HO_{2_{sh}}^{eq}}$, depends essentially on the season and latitude. Comparing with Figure 1~~,~~ one can see, that it ~~repeats well~~reproduces many features of $z_{HO_{2_{sh}}^{eq}}$ at low and middle latitudes. In particular, $z_{HO_{2_{sh}}^{eq}}$ varies in the interval between 73 and 85 km, as in the case of $z_{HO_2^{eq}}$. In the middle latitudes~~,~~ ~~$z_{HO_{2_{sh}}^{eq}}$~~$z_{HO_{2_{sh}}^{eq}}$ in summer is several km higher than in winter. Near the equator~~,~~ $z_{HO_{2_{sh}}^{eq}}$ demonstrates the weakest annual variations and varies in the range of 81-83 km. So, one can conclude, that the exclusion of a number of reactions does not lead to significant changes in the space-time distributions of the HO_2 equilibrium.

~~The~~ Figure ~~10~~6 plots height-latitude cross sections for the $< OH/OH_{sh}^{eq} >$ ratio for each month. As in the previous case, this is the lower ~~border~~boundary of the equilibrium area, where~~,~~ according to condition (1~~),~~) $OH \approx OH_{sh}^{eq}$ with good precision. The dependence of the ~~border~~boundary height, $z_{OH_{sh}^{eq}}$, on the season and latitude mainly repeats ~~mainly~~ the behavior of $z_{HO_{2_{sh}}^{eq}}$. In particular~~,~~ $z_{OH_{sh}^{eq}}$ varies in the interval between 73 and 85 km. At middle latitudes~~,~~ $z_{OH_{sh}^{eq}}$ in summer is several km higher than in winter. Near the equator~~,~~ $z_{OH_{sh}^{eq}}$ also demonstrates the weakest annual variations and varies in the range of 81-83

km. Nevertheless, in some cases~~,~~ the OH equilibrium ~~border~~boundary lies slightly higher than the HO_2 ~~border~~boundary. In particular~~,~~ it can be seen in April-August above 50ºS, which can be explained by the difference between HO_2 and OH lifetimes ($\tau_{HO_2} < \tau_{OH}$), mainly~~,~~ due to $k_{18} > k_{17}$. Comparing with Figure 2, one can see ~~that~~ the exclusion of the mentioned reactions from consideration results in the absence of the OH equilibrium areas at the low and middle mesosphere altitudes, as expected.

6 The ~~criterions~~criteria for HO_2 and OH equilibrium validity in the upper mesosphere and lower thermosphere

~~Let~~Firstly we determine HO_2 and OH lifetimes and the local time scales of $HO_{2_{sh}}^{eq}$ and OH_{sh}^{eq}, according to Section 2.

From ~~(8~~Eqs. (2-3) and (9), HO_2 lifetime and the local time scales of $HO_{2_{sh}}^{eq}$ are as follows:

$$\tau_{HO_2} = \frac{1}{k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H}, \quad (10$$

$$\frac{1}{k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H}, \quad (11)$$

$$\tau_{HO_{2_{sh}}^{eq}} = \frac{HO_{2_{sh}}^{eq}}{|dHO_{2_{sh}}^{eq}/dt|}. \quad (~~11~~12)$$

~~Let~~Then we find the expression for $dHO_{2_{sh}}^{eq}/dt$:

$$\frac{dHO_{2_{sh}}^{eq}}{dt} = \frac{k_{18}\cdot k_{20}\cdot M\cdot O_2\cdot\frac{d}{dt}(\frac{H}{O})\cdot O^2}{(k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H)^2} = -\frac{k_{18}\cdot k_{20}\cdot M\cdot O_2\cdot\frac{d}{dt}(\frac{O}{H})\cdot H^2}{(k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H)^2}. \quad (12$$

$$\frac{k_{18}\cdot k_{20}\cdot M\cdot O_2\cdot\frac{d}{dt}(\frac{O}{H})\cdot H^2}{(k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H)^2}. \quad (13)$$

Kulikov et al. (2023a) analyzed ~~analytically~~ the local nighttime evolution of O and H within the framework of pure HO_x – O_x chemistry and found the expression for $\frac{d}{dt}(\frac{O}{H})$:

$$\frac{d}{dt}\left(\frac{O}{H}\right) = -2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right) - k_{21}\cdot O_3 - k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\frac{O}{H}. \quad (~~13~~14)$$

Thus, ~~the expression (12~~Eq. (13) can be rewritten in the following form:

$$\frac{dHO_{2_{sh}}^{eq}}{dt} = \frac{k_{18}\cdot k_{20}\cdot M\cdot O_2\cdot H^2\cdot\left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)}{(k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H)^2}.$$

(14

$$\frac{k_{18}\cdot k_{20}\cdot M\cdot O_2\cdot H^2\cdot\left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)}{(k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H)^2}. \quad (15)$$

By combining (8), (11Eqs. (9), (12), and (1415) we obtain the expression for the local time scales of $HO_{2_{sh}}^{eq}$:

$$\tau_{HO_{2_{sh}}^{eq}}\tau_{HO_{2_{sh}}^{eq}} = \frac{(k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H)}{k_{18}\cdot H\cdot\left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)}\cdot\frac{(k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H)}{k_{18}\cdot H\cdot\left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)}$$

(1516

)

Thus, taking into account (3), (10Eqs. (4), (11) and (1516), the criterion for HO_2 equilibrium validity is written in the form:

$$Crit_{HO_2} = \frac{\tau_{HO_2}}{\tau_{\tau_{HO_{2_{sh}}^{eq}}}} = \frac{k_{18}\cdot H\cdot\left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)}{(k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H)^2} \leq 0.1.$$

(16

$$\frac{k_{18}\cdot H\cdot\left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)}{(k_{18}\cdot O+(k_{14}+k_{15}+k_{16})\cdot H)^2} \leq 0.1. \quad (17)$$

We calculated $Crit_{HO_2}$, using the global 3D chemical transport model, and included the zonally and monthly averaged lines $< Crit_{HO_2} >= 0.1$ in Figure 95 (see magenta lines). One can see that, depending on the month, each redmagenta line well reproduces well the lower borderboundary of the main OHHO$_2$ equilibrium area and repeatsfollows almost all its features and variations. Note, that, in zerothe zeroth order approximation, the criterion (1617) can be simplified as

$$Crit_{HO_2} \approx \left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)\left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)\cdot\frac{H}{k_{18}\cdot O^2}\leq 0.1.$$

(1718

)

From (9Eqs. (2-3) and (10), OH lifetime and the local time scales of OH_{sh}^{eq} are as follows:

$$\tau_{OH} = \frac{1}{k_{17}\cdot O}\frac{1}{k_{17}\cdot O},$$

(1819

)

$$\tau_{OH_{sh}^{eq}} = \frac{OH_{sh}^{eq}}{|dOH_{sh}^{eq}/dt|}.$$

(~~19~~20)

Before determining the expression for dOH_{sh}^{eq}/dt~~, first of all,~~ one should ~~to~~ keep in mind, that the expression (~~9~~10) depends on the HO_2 concentration. ~~Above~~As previously mentioned, ~~that~~ near and above the OH equilibrium ~~border,~~boundary HO_2 is in equilibrium ($HO_2 \approx HO_{2_{sh}}^{eq}$) and we can use ~~expression~~ (~~8~~Eq. (9)). In view of $k_{18} \cdot O \gg (k_{14} + k_{15} + k_{16}) \cdot H$,

$$HO_{2_{sh}}^{eq} \approx \frac{k_{20} \cdot H \cdot M \cdot O_2}{k_{18} \cdot O}\left(1 - \frac{(k_{14}+k_{15}+k_{16}) \cdot H}{k_{18} \cdot O}\right).$$

(~~20~~21)

The substitution of (~~20~~Eq. (21)) into (~~9~~Eq. (10)) yields:

$$OH_{sh}^{eq} = k_{20} \cdot H \cdot M \cdot O_2 \cdot \frac{\left(1+\frac{2 \cdot k_{14} \cdot H}{k_{18} \cdot O}\right) \cdot \left(1-\frac{(k_{14}+k_{15}+k_{16}) \cdot H}{k_{18} \cdot O}\right)}{k_{17} \cdot O} + \frac{k_{21} \cdot H \cdot O_3}{k_{17} \cdot O} \approx$$

$$\frac{k_{20} \cdot H \cdot M \cdot O_2}{k_{17} \cdot O} \cdot \left(1 + \frac{\cancel{(k_{14}-k_{15}-k_{16}) \cdot H}}{\cancel{k_{18} \cdot O}} \frac{(k_{14}-k_{15}-k_{16}) \cdot H}{k_{18} \cdot O}\right) + \frac{k_{21} \cdot H \cdot O_3}{k_{17} \cdot O}$$

(~~21~~22)

Thus, the expression for dOH_{sh}^{eq}/dt is:

$$\frac{dOH_{sh}^{eq}}{dt} = \frac{d}{dt}\left(\frac{H}{O}\right) \cdot \left(\frac{k_{20} \cdot M \cdot O_2}{k_{17}} \cdot \left(1 + \frac{2 \cdot (k_{14}-k_{15}-k_{16}) \cdot H}{k_{18} \cdot O}\right) + \frac{k_{21} \cdot O_3}{k_{17}}\right) + \frac{k_{21} \cdot H \cdot}{k_{17} \cdot O} \frac{dO_3}{dt}.$$

(~~22~~23)

Taking into account (~~13~~Eq. (14)) and the differential equation for O_3 time evolution:

$$\frac{dO_3}{dt} = k_{12} \cdot M \cdot O_2 \cdot O - k_{21} \cdot H \cdot O_3,$$

the expression (~~21~~23) can be rewritten in following form:

$$\frac{dOH_{sh}^{eq}}{dt} =$$

$$\cancel{(2 \cdot k_{20} \cdot M \cdot O_2 \cdot \left(1 - \frac{k_{15}+k_{16}}{k_{18}}\right) + k_{21} \cdot O_3 + k_{12} \cdot M \cdot O_2 \cdot \frac{O}{H}) \cdot \frac{H^2}{O^2}\left(\frac{k_{20} \cdot M \cdot O_2}{k_{17}} \cdot \left(1 + \frac{2 \cdot (k_{14}-k_{15}-k_{16}) \cdot H}{k_{18} \cdot O}\right) +}$$

$$\cancel{\frac{k_{21} \cdot O_3}{k_{17}}}\Big) = \frac{(2 \cdot k_{20} \cdot M \cdot O_2 \cdot \left(1 - \frac{k_{15}+k_{16}}{k_{18}}\right) + k_{21} \cdot O_3 + k_{12} \cdot M \cdot O_2 \cdot \frac{O}{H}) \cdot H^2}{O^2} \cdot \left(\frac{k_{20} \cdot M \cdot O_2}{k_{17}} \cdot \left(1 + \frac{2 \cdot (k_{14}-k_{15}-k_{16}) \cdot H}{k_{18} \cdot O}\right) + \frac{k_{21} \cdot O_3}{k_{17}}\right) +$$

$$\frac{\cancel{k_{21} \cdot H \cdot (k_{12} \cdot M \cdot O_2 \cdot O - k_{21} \cdot H \cdot O_3)}}{\cancel{k_{17} \cdot O}} \frac{k_{21} \cdot H \cdot (k_{12} \cdot M \cdot O_2 \cdot O - k_{21} \cdot H \cdot O_3)}{k_{17} \cdot O}.$$

(2324)

Thus, by combining (3), (18Eqs. (4), (19), (2120), (22), and (2324) we obtain the expression for the criterion for OH equilibrium validity:

$$Crit_{OH} = \frac{\tau_{OH}}{\tau_{OH_{sh}^{eq}}} = \frac{1}{k_{17}\cdot O}\cdot\left(\left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)\cdot\frac{H}{O}\cdot\left(k_{20}\cdot M\cdot O_2\cdot\left(1+\frac{2\cdot(k_{14}-k_{15}-k_{16})\cdot H}{k_{18}\cdot O}\right)+k_{21}\cdot O_3\right)+k_{21}\cdot(k_{12}\cdot M\cdot O_2\cdot O-k_{21}\cdot H\cdot O_3)\right)/(k_{20}\cdot M\cdot O_2\cdot(1+\frac{(k_{14}-k_{15}-k_{16})\cdot H}{k_{18}\cdot O})+k_{21}\cdot O_3)\leq 0.1.$$

(24

$$\frac{\left(\left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3\cdot\frac{H}{O}+k_{12}\cdot M\cdot O_2\right)\cdot\left(k_{20}\cdot M\cdot O_2\cdot\left(1+\frac{2\cdot(k_{14}-k_{15}-k_{16})\cdot H}{k_{18}\cdot O}\right)+k_{21}\cdot O_3\right)+k_{21}\cdot(k_{12}\cdot M\cdot O_2\cdot O-k_{21}\cdot H\cdot O_3)\right)}{k_{17}\cdot O\cdot(k_{20}\cdot M\cdot O_2\cdot(1+\frac{(k_{14}-k_{15}-k_{16})\cdot H}{k_{18}\cdot O})+k_{21}\cdot O_3)}\leq$$

0.1. (25)

We calculated $Crit_{OH}$, using the global 3D chemical transport model, and included the zonally and monthly averaged lines $< Crit_{OH} >= 0.1$ in Figure 106 (see magenta lines). One can see that, depending on the month, redthe magenta line almost everywhere reproduces the lower borderboundary of the OH equilibrium area and repeats mainly its features and variations. Nevertheless, there are a few (by latitude) narrow areas (in April-August near 70ºS and in October-December near 70ºN)), where the criterion gives a few km lower position of the OH equilibrium boundary, that is going to bethese are discussed below.in the next section. Note, that our numerical analysis shows that, in zerothe zeroth order approximation, the criterion (2425) can be simplified as:

$$Crit_{OH} \approx \left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)\left(2\cdot k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3+k_{12}\cdot M\cdot O_2\cdot\frac{O}{H}\right)\cdot\frac{H}{k_{17}\cdot O^2}\leq 0.1.$$

(2526)

7 Discussion

Let'sWe now discuss obtained results and their possible applications.

Pay attention to the fact, that 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 HO_2 equilibrium conditions are fulfilled at χ>95°. Evidently, during the

processing of the measurement data, taking twilight χ in (95°,105°) range into account extends the latitude range of OH and HO_2 equilibria application and allows us to include a noticeable part of the data into 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 HO_2 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. Mind, that at night O and H tend to decrease due to the shutdown of the O_x and HO_x family photochemical sources, so τ_{HO_2} and τ_{OH} increase. Thus, analyzing the measurement data one can apply more stringent conditions:

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

The main results were obtained using a 3D model, where temperature and wind distributions are 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, calculated 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 HO_2, especially at low latitudes, showed that our criteria reproduce quite well the local variations of the OH and HO_2 equilibrium boundaries in such conditions.

We evaluated the sensitivity of the presented HO_2 and OH criteria ($Crit_{HO_2}$ and $Crit_{OH}$) to the uncertainties of characteristics, involved in the expressions (17) and (25). The local heights of the OH and HO_2 equilibrium boundaries (${z_{HO_2}}^{crit}$ 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, O_3, M, O_2 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 O_3, 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 of total uncertainties in 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, that these values are comparable with the typical height

resolution of satellite data. The latter allows us to consider our criteria as a robust instrument for equilibrium condition validation. 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.

As noted, ~~Figures 9-10 present~~Figs. 5-6 represent an interesting peculiarity. At the middle latitudes~~,~~ summer $z_{HO_{2_{sh}}^{eq}}$ and $z_{OH_{sh}^{eq}}$ are ~~several km~~remarkably higher than winter ones. Recently ~~(~~, Kulikov et al~~., ~~(2023b) found such a feature ~~was found~~ in the evolution of nighttime ozone chemical equilibrium boundary, derived from SABER/TIMED data, ~~whichwas~~which was accompanied by the same variation of the transition zone ~~dividing,~~ separating deep and weak photochemical oscillations of O and H, caused by the diurnal variations of solar radiation. ~~Kulikov et al. (2023b)~~ The authors analyzed this effect ~~analytically and~~ near and below the transition zone. It was shown firstly, 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. Secondly, during the summer the daytime O/H at the middle latitudes is remarkably less than the one in winter. Consequently, summer values of τ_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 $z_{HO_{2_{sh}}^{eq}}$ and $z_{OH_{sh}^{eq}}$ can be explained by the ~~markedly lower values of the O and H nighttime evolution times in summer than in winter by virtue, mainly, of the lower values of the O/H ratio during the night, which, in turn, is determined by the daytime photochemistry. At middle, the ozone boundary varies within 4-5 km interval above 80 km, whereas the range of OH and HO_2 boundaries variations is 72-85 km (see Figures 9-10). In the case of ozone, its criterion for equilibrium validity (see (5) in Kulikov et al. (2023b)) is as follows:~~season difference in O diurnal evolution at these latitudes.

~~$$Crit_{O_3} = 2\frac{k_{12}\cdot O_2\cdot M}{k_{21}}\left(k_{20}\cdot M\cdot O_2\cdot\left(1-\frac{k_{15}+k_{16}}{k_{18}}\right)+k_{21}\cdot O_3\right)\cdot\frac{1}{k_{21}\cdot H\cdot O_3}\leq 0.1. \quad (26)$$~~

~~At $O_3 \approx O_3{}^{eq} = \frac{k_{12}\cdot M\cdot O_2\cdot O}{k_{21}\cdot H}$, one can see that $Crit_{O_3}\sim\frac{1}{O}$. It is follows from simplified expressions (17) and (25) that $Crit_{HO_2}$ and $Crit_{OH}$ are proportional to $\frac{H}{O^2}$. Such dependence leads to a stronger annual variation of OH and HO_2 equilibrium boundaries than in the case of O_3.~~

As noted, there are a few narrow areas near 70ºS~~,~~/N (Figure ~~10)~~6), where the criterion (25) does not ~~agree~~correspond well ~~with~~to the OH equilibrium boundary. Our analysis revealed, that the main reason is neglecting the reaction OH+CO → H+CO_2 as the source of H in the corresponding differential equation of its chemical balance. In order to improve the criterion~~,~~ we revised the derivation of expression (~~17~~14) for $\frac{d}{dt}\left(\frac{O}{H}\frac{O}{H}\right)$ following to Kulikov et al. (2023a):

$$\frac{d}{dt}\left(\frac{O}{H}\right) = -2 \cdot k_{20} \cdot M \cdot O_2 \cdot \left(1 - \frac{k_{15}+k_{16}}{k_{18}}\right) - k_{21} \cdot O_3 - k_{12} \cdot M \cdot O_2 \cdot \frac{O}{H} - \frac{k_{32} \cdot CO}{k_{17} \cdot H} \cdot (k_{20} \cdot M \cdot O_2 \cdot (1 + \frac{(k_{14}-k_{15}-k_{16}) \cdot H}{k_{18} \cdot O}) + k_{21} \cdot O_3)).$$

(~~27~~29)

As ~~the~~a result~~,~~ the corrected criterion for OH equilibrium validity is as follows:

~~$$Crit_{OH}{}^{m} = \frac{1}{k_{17} \cdot O} \cdot \left(\left(2 \cdot k_{20} \cdot M \cdot O_2 \cdot \left(1 - \frac{k_{15}+k_{16}}{k_{18}}\right) + k_{21} \cdot O_3 + k_{12} \cdot M \cdot O_2 \cdot \frac{O}{H} + \frac{k_{32} \cdot CO}{k_{17} \cdot H} \cdot (k_{20} \cdot M \cdot O_2 \cdot (1+k14-k15-k16 \cdot Hk18 \cdot O) + k21 \cdot O3)) \cdot HO \cdot k20 \cdot M \cdot O2 \cdot 1 + 2 \cdot k14 - k15 - k16 \cdot Hk18 \cdot O + k21 \cdot O3 + k21 \cdot k12 \cdot M \cdot O2 \cdot O - k21 \cdot H \cdot O3 / (k20 \cdot M \cdot O_2 \cdot (1 + \frac{(k_{14}-k_{15}-k_{16}) \cdot H}{k_{18} \cdot O}) + k_{21} \cdot O_3) \leq 0.1. \quad (28)$$~~

$$Crit_{OH}{}^{m} = \frac{2 \cdot k_{20} \cdot M \cdot O_2 \cdot \left(1 - \frac{k_{15}+k_{16}}{k_{18}}\right) + k_{21} \cdot O_3 + k_{12} \cdot M \cdot O_2 \cdot \frac{O}{H} + \frac{k_{32} \cdot CO}{k_{17} \cdot H} \cdot (k_{20} \cdot M \cdot O_2 \cdot (1 + \frac{(k_{14}-k_{15}-k_{16}) \cdot H}{k_{18} \cdot O}) + k_{21} \cdot O_3))}{k_{17} \cdot O \cdot (k_{20} \cdot M \cdot O_2 \cdot (1 + \frac{(k_{14}-k_{15}-k_{16}) \cdot H}{k_{18} \cdot O}) + k_{21} \cdot O_3)} \cdot \frac{H}{O} \cdot \left(k_{20} \cdot M \cdot O_2 \cdot \left(1 + \frac{2 \cdot (k_{14}-k_{15}-k_{16}) \cdot H}{k_{18} \cdot O}\right) + k_{21} \cdot O_3\right) + \frac{k_{21} \cdot (k_{12} \cdot M \cdot O_2 \cdot O - k_{21} \cdot H \cdot O_3)}{k_{17} \cdot O \cdot (k_{20} \cdot M \cdot O_2 \cdot (1 + \frac{(k_{14}-k_{15}-k_{16}) \cdot H}{k_{18} \cdot O}) + k_{21} \cdot O_3)} \leq 0.1 \quad (30)$$

We calculated this criterion, using the global 3D chemical transport model and included the zonally and monthly averaged lines $< Crit_{OH}{}^{m} >= 0.1$ on the OH equilibrium maps (see Figure ~~11~~8). One can see that ~~including~~, the inclusion of this additional term actually eliminates the noted discrepancy between OH boundary and criterion. But~~,~~ the application of this criterion requires CO data.

As noted in the Introduction, the conditions of nighttime OH and HO_2 ~~equilibriums~~equilibria together with one for O_3 equilibrium and their analytical criteria constitute ~~the~~a useful tool for ~~to~~ retrieval of these components or other characteristics (for example, O and H) from measured data. At the altitudes of upper mesosphere – lower thermosphere~~,~~ these conditions can be applied, for example, to MLS/Aura database (measured characteristics: OH, HO_2, O_3, and CO), SMILES (HO_2 and O_3), SCIAMACHY ($O(^1S)$ green-line, O_2 A-band, and OH Meinel band emissions), SABER/TIMED (O_3, OH Meinel band emissions at 2.0 μm (9→7 and 8→6 bands) and at 1.6 μm (5→3 and 4→2 bands)) and other, including ~~to improve~~improvement of existing retrieval approaches. In particular, Panka et al. (2021) proposed the method of simultaneous derivation of O and OH at the levels v=0-9 from SABER data (volume emission rates at 2.0 and 1.6 μm~~),~~ $VER_{2\mu m}$ and $VER_{1.6\mu m}$) at 80-100 km, taking into account the equilibrium condition for all states of OH. Such approach is valid for ~~excited~~excited states due to ~~its~~their very ~~low~~short lifetimes determined by radiative transitions and quenching with O_2, N_2, and O. In the case of the OH ground state~~,~~ its ~~lifetimes~~lifetime is determined by the reaction OH+O → H+O_2 only. It means, that

Panka et al. (2021) used an equilibrium condition for total OH, which, as one can see from Figure 6, may be significantly disrupted above 80 km ~~in certain~~. On the other hand, there are latitude ranges and ~~seasons, as one can see from Figure 8. In order to check this assumption, we processed~~months, when the OH equilibrium boundary drops remarkably below 80 km. Moreover, the Panka et al. ~~(2021)~~method requires external data ~~(~~about HO_2, since the reaction HO_2+O~~,~~ → OH~~(v=9),~~ +O_2~~, N_2, and temperature profiles at 80-100 km)~~ becomes the important source for ~~2009 and calculated local profiles of $Crit_{OH}$ according to criterion (24). One can see this criterion depends of O, H, and O_3. Thus, the O_3 data was taken from SABER data collocated (via the orbit number) with the~~ OH below 87 km (Panka et al~~. profiles in time and space. The H data was derived with the use of the equilibrium equation for OH(v=9):~~., 2021; see also Figure 4 in our paper).

~~$a_7 \cdot O_3 \cdot H = OH(9) \cdot (a_1 + a_2 \cdot N_2 + a_3 \cdot O_2 + (a_4 + a_5 + a_6) \cdot O)$, (29)~~

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 HO_2 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_{1-7}~~a_{1-6} are the constant rates of the processes OH(~~9~~v) → OH(v′≤v≤~~8~~) + hν, OH(~~9~~v) +O_2 → OH(v<v′) + O_2, OH(v) +N_2 → OH(~~8~~v<v′) + N_2, OH(~~9) +O_2 → OH(v≤8) + O_2, OH(9~~v) +O(^{3}P) → OH(v′≤v≤~~4~~5) + O(^{1}D), OH(~~9~~v) +O(^{3}P) → OH(v′<v≤~~8~~) + O(^{3}P), and OH(v) +O(^{3}P) → H + O_2~~, and H + O_3 → O_2 + OH(9),~~ respectively. ~~The values of a_{2-7} correspond to the Panka et al. (2021) model (see Table 1 there), the Einstein coefficients for OH(v=9) were taken from Brooke et al. (2016). Due to the strong air concentration dependence $Crit_{OH}$ decreases rapidly~~Take into consideration, that this system includes 13 equations with ~~the height. From each $Crit_{OH}$ profile~~13 unknown variables. Therefore, the solution to the system for a single set of the SABER measurements (simultaneously measured profiles of O_3, 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 HO_2. By applying the criteria (17) and (25) to obtained O and H profiles, we ~~determined the local height position of the OH equilibrium boundary ($z_{OH_{sh}^{eq}}$) according to the condition $Crit_{OH} = 0.1$. It was revealed that $Crit_{OH} < 0.1$ throughout the entire altitude range for most profiles. The Figure 12 plots the~~

found values of $z_{OH_{5\pi}^{eq}}$ above 80 km in different months. One can see that, in accordance of the Panka et al. data,verify the local height position of the OH equilibrium boundary can rise up to 87 km. Moreover, the Panka et al. method requires external data about HO_2 since the reaction $HO_2+O \rightarrow OH+O_2$ become the important source for OH below 87 km (Panka et al., 2021; see also Figure 5 in our paper). Note that thefulfillment of OH and HO_2 equilibrium condition (8) depends on Hconditions and O only and can be used withindetermine the generalheight, below which the resulting profiles should be cut. More advanced retrieval procedure of O, H, OH(v=0-9), and HO_2would be statistical, based on Bayesian theorem, taking into account the criteria (16) and (24).uncertainties in measurement data and rate constants. Similarly, 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 extended work.

8 Conclusions

The presented analysis shows, that there are extended areas in mesosphere and lower thermosphere, where nighttime HO_2 and OH are close to their local equilibrium concentrations, determined mainly by the reactionreactions between HO_x – O_x components among themselves and with H_2O_2, N, NO, NO_2, and CO. In upper mesosphere – lower thermosphere, the shortened expressions for their local equilibrium concentrations are valid, including the HO_x – O_x chemistry only. These conditions describesdescribe the HO_2 and OH equilibrium from the top to the some lower bordersboundaries, the altitude position of which vary in the interval between 73 and 85 km and depends essentially on the season and latitude. We proposed analytical criteria, which almost everywhere well reproduces quite well the main features of these bordersboundaries. Due to weak sensitivity to uncertainties of reaction rates and variables, these criteria can be considered a robust instrument for HO_2 and OH equilibrium validation. The obtained results allow extending the abilities of the Panka et al. (2021) method of retrieval ofto retrieve unmeasured components from SABER data. The simultaneous application of OH and HO_2 equilibrium conditions to the SABER data (O_3, volume emission rates at 2.0 and 1.6 μm) together with the OH and HO_2 criteria (16) and (24) to control this equilibrium validity is goingallows us to retrieve all unknown HO_x – O_x components (O, H, OH, and HO_2), extending) and to extend the altitude range of retrieval downward below 80 km and without external information.

Data availability. ~~The Panka et al.~~CMAM data are obtained from the ~~SABER~~ website (https://~~saber.gats-inc.com).~~ climate-modelling.canada.ca/climatemodeldata/cmam/cmam30/, last access: 18 May 2024).

Code availability. Code is available upon request.

Author contributions. Conceptualization: MK~~ and,~~ MB~~ carried out the data processing and analysis and wrote the manuscript.,~~ AC, SD, ~~and AM contributed to reviewing the article~~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: AF.

Competing interests. The authors declare ~~that they have~~ no conflict of interest.

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Supplement link:

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Table 1. List of reactions included in 3-d chemical transport model with the corresponding reaction rates taken from Burkholder et al. (2020).

1	$O(^1D)+O_2 \rightarrow O+O_2$	24	$H+OH+N_2 \rightarrow H_2O+N_2$	47	$NO+O_3 \rightarrow NO_2+O_2$
2	$O(^1D)+N_2 \rightarrow O+N_2$	25	$OH+H_2 \rightarrow H_2O+H$	48	$NO_2+O_3 \rightarrow NO_3+O_2$
3	$O(^1D)+O_3 \rightarrow O_2+2O$	26	$OH+OH \rightarrow H_2O+O$	49	$N+OH \rightarrow NO+H$
4	$O(^1D)+O_3 \rightarrow 2O_2$	27	$OH+OH+M \rightarrow H_2O_2+M$	50	$NO+HO_2 \rightarrow NO_2+OH$
5	$O(^1D)+N_2O \rightarrow 2NO$	28	$OH+HO_2 \rightarrow H_2O+O_2$	51	$H+NO_2 \rightarrow OH+NO$
6	$O(^1D)+N_2O \rightarrow N_2+O_2$	29	$H_2O_2+OH \rightarrow H_2O+HO_2$	52	$NO_3+NO \rightarrow 2NO_2$
7	$O(^1D)+H_2O \rightarrow 2OH$	30	$HO_2+HO_2 \rightarrow H_2O_2+O_2$	53	$N+NO \rightarrow N_2+O$
8	$O(^1D)+H_2 \rightarrow H+OH$	31	$HO_2+HO_2+M \rightarrow H_2O_2+O_2+M$	54	$N+NO_2 \rightarrow N_2O+O$
9	$O(^1D)+CH_4 \rightarrow CH_3+OH$	32	$OH+CO \rightarrow H+CO_2$	55	$O_2+h\nu \rightarrow 2O$
10	$O(^1D)+CH_4 \rightarrow H_2+CH_2O$	33	$CH_4+OH \rightarrow CH_3+H_2O$	56	$O_2+h\nu \rightarrow O+O(^1D)$
11	$O+O+M \rightarrow O_2+M$	34	$CH_3+O_2 \rightarrow CH_3O_2$	57	$O_3+h\nu \rightarrow O_2+O$
12	$O+O_2+M \rightarrow O_3+M$	35	$CH_3+O \rightarrow CH_2O+H$	58	$O_3+h\nu \rightarrow O_2+O(^1D)$
13	$O+O_3 \rightarrow O_2+O_2$	36	$CH_3O_2+NO \rightarrow CH_3O+NO_2$	59	$N_2+h\nu \rightarrow 2N$
14	$H+HO_2 \rightarrow 2OH$	37	$CH_3O+O_2 \rightarrow CH_2O+HO_2$	60	$NO+h\nu \rightarrow N+O$
15	$H+HO_2 \rightarrow H_2O+O$	38	$CH_2O \rightarrow H_2+CO$	61	$NO_2+h\nu \rightarrow NO+O$
16	$H+HO_2 \rightarrow H_2+O_2$	39	$CH_2O \rightarrow H+CHO$	62	$N_2O+h\nu \rightarrow N_2+O(^1D)$
17	$OH+O \rightarrow H+O_2$	40	$CHO+O_2 \rightarrow HO_2+CO$	63	$N_2O+h\nu \rightarrow N+NO$
18	$HO_2+O \rightarrow OH+O_2$	41	$O_3+N \rightarrow NO+O_2$	64	$NO_3+h\nu \rightarrow NO_2+O$
19	$H_2O_2+O \rightarrow OH+HO_2$	42	$NO_3+O \rightarrow NO_2+O_2$	65	$H_2O+h\nu \rightarrow H+OH$
20	$H+O_2+M \rightarrow HO_2+M$	43	$O+NO+M \rightarrow NO_2+M$	66	$H_2O_2+h\nu \rightarrow 2OH$
21	$H+O_3 \rightarrow OH+O_2$	44	$NO_2+O \rightarrow NO+O_2$	67	$CH_4+h\nu \rightarrow CH_2+H_2$
22	$OH+O_3 \rightarrow O_2+HO_2$	45	$NO_2+O+M \rightarrow NO_3+M$	68	$CH_4+h\nu \rightarrow CH+H_2+H$
23	$HO_2+O_3 \rightarrow OH+2O_2$	46	$N+O_2 \rightarrow NO+O$	69	$CO_2+h\nu \rightarrow CO+O$

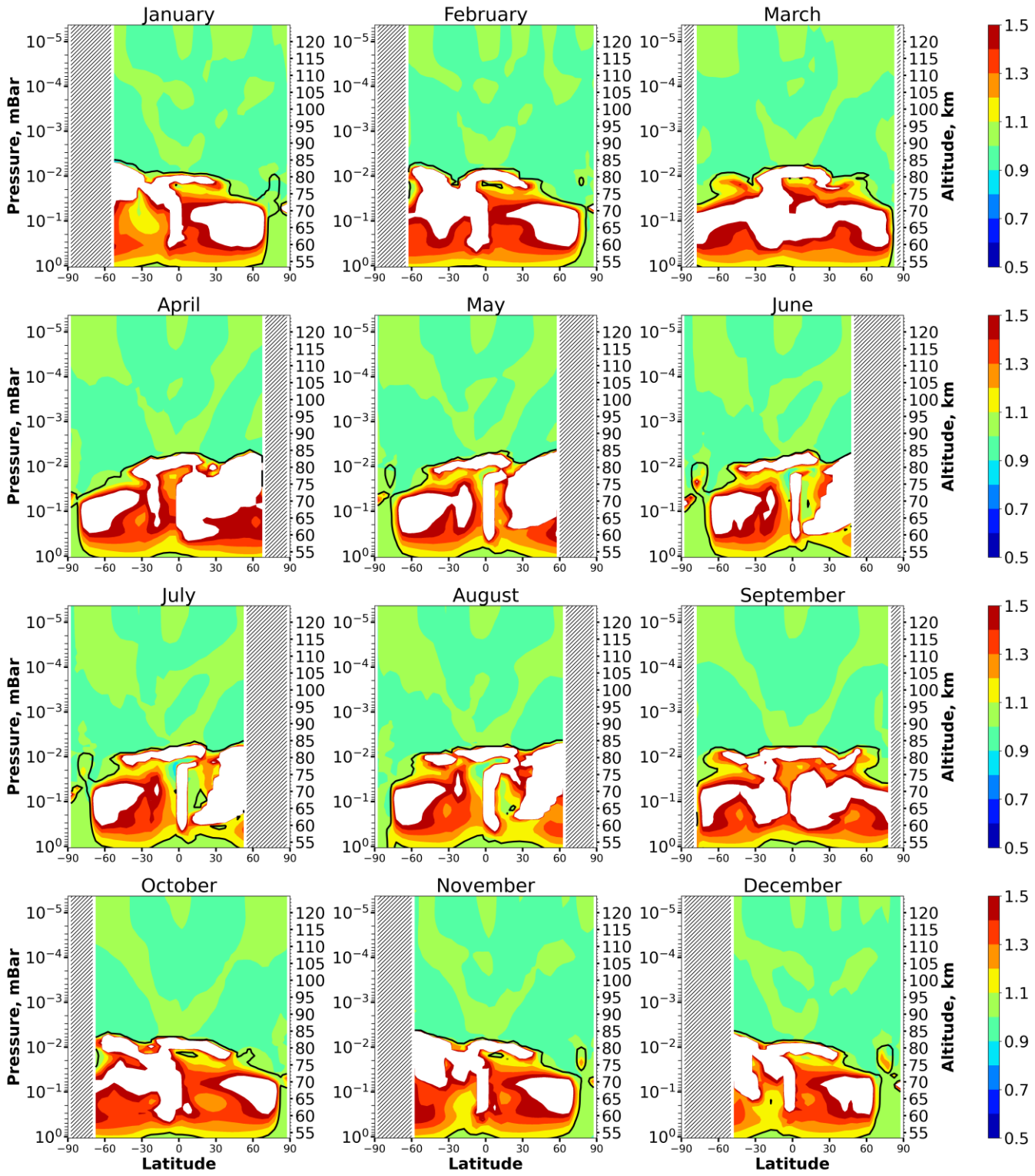


Figure 1. Nighttime mean and monthly averaged $HO_2/{HO_2}^{eq}$~~.~~, where ${HO_2}^{eq}$ is equilibrium concentration determined by Eq. (5). Black line shows the ~~border~~boundary of HO_2 equilibrium according to condition (1). The stippling corresponds to χ<105°. The white area represents the $< HO_2/{HO_2}^{eq} >$ ratio outside the [0.5, 1.5] interval.

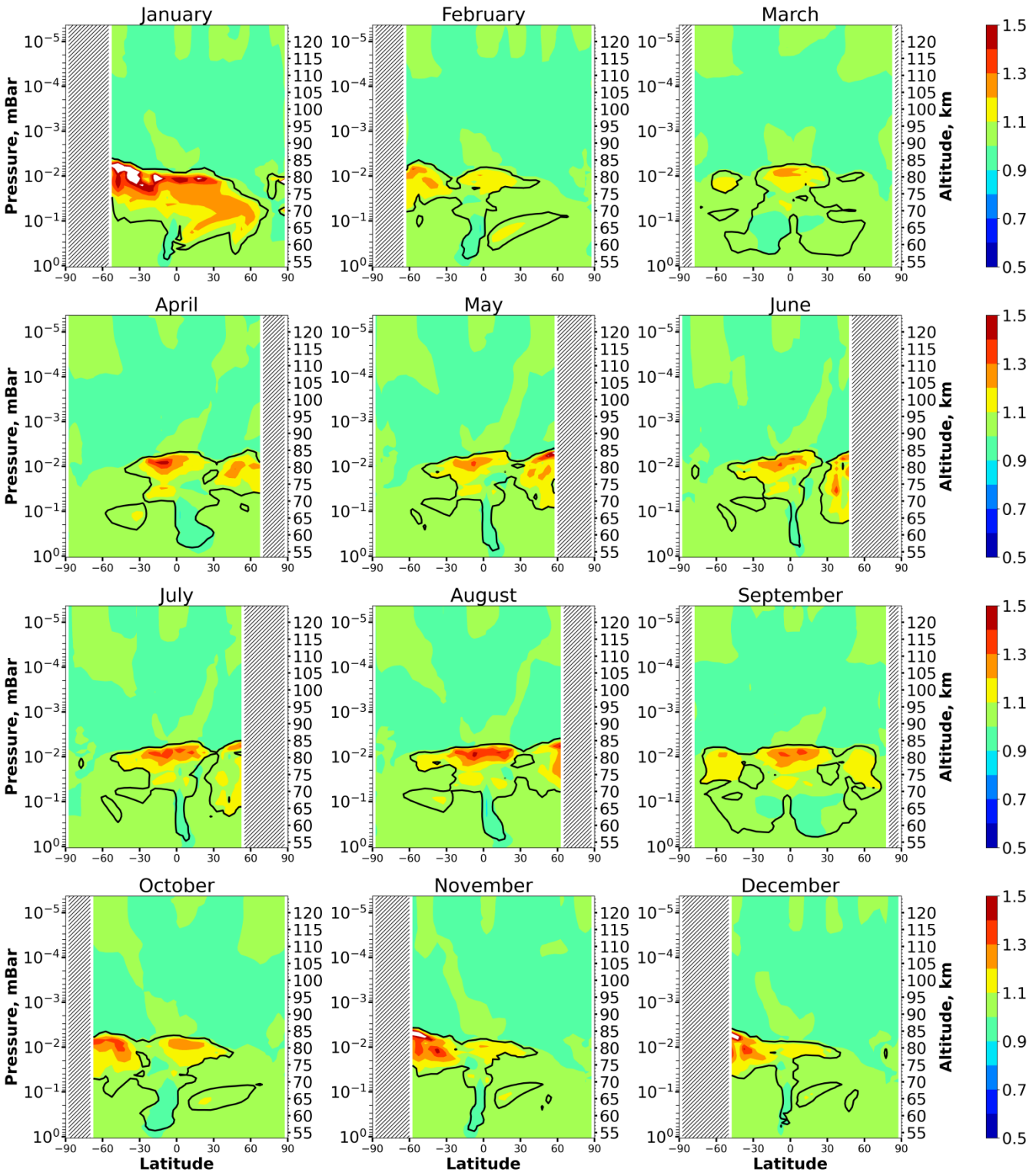
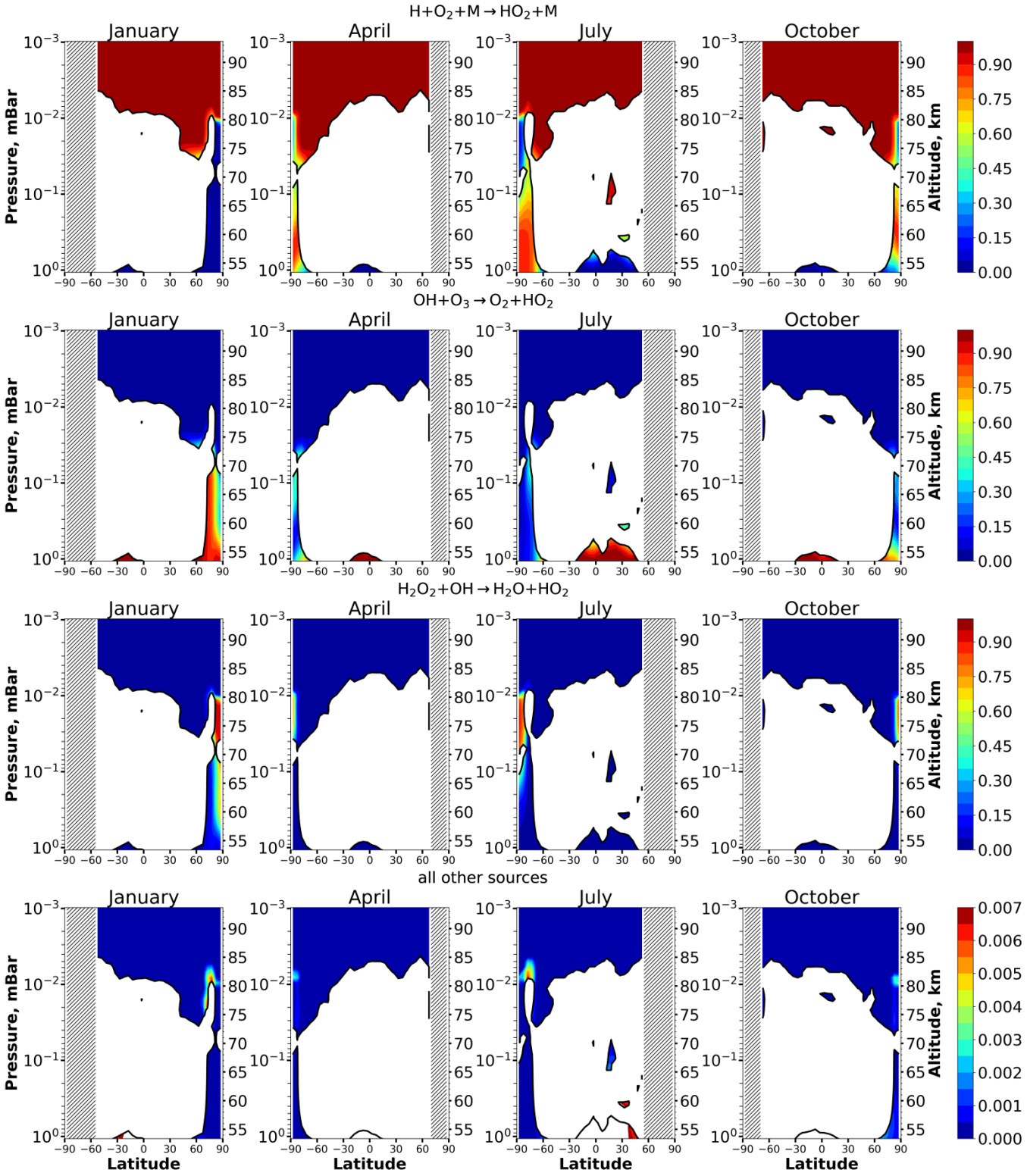


Figure 2. Nighttime mean and monthly averaged OH/OH^{eq}~~.~~, where OH^{eq} is equilibrium concentration determined by Eq. (6). Black line shows the ~~border~~boundary of OH equilibrium according to condition (1). The stippling corresponds to χ<105°. The white area represents the $< OH/OH^{eq} >$ ratio outside the [0.5, 1.5] interval.


H+O2+M→HO2+M
OH+O3→O2+HO2
H2O2+OH→H2O+HO2
all other sources
January
April
July
October
Pressure, mBar
Altitude, km
Latitude

803

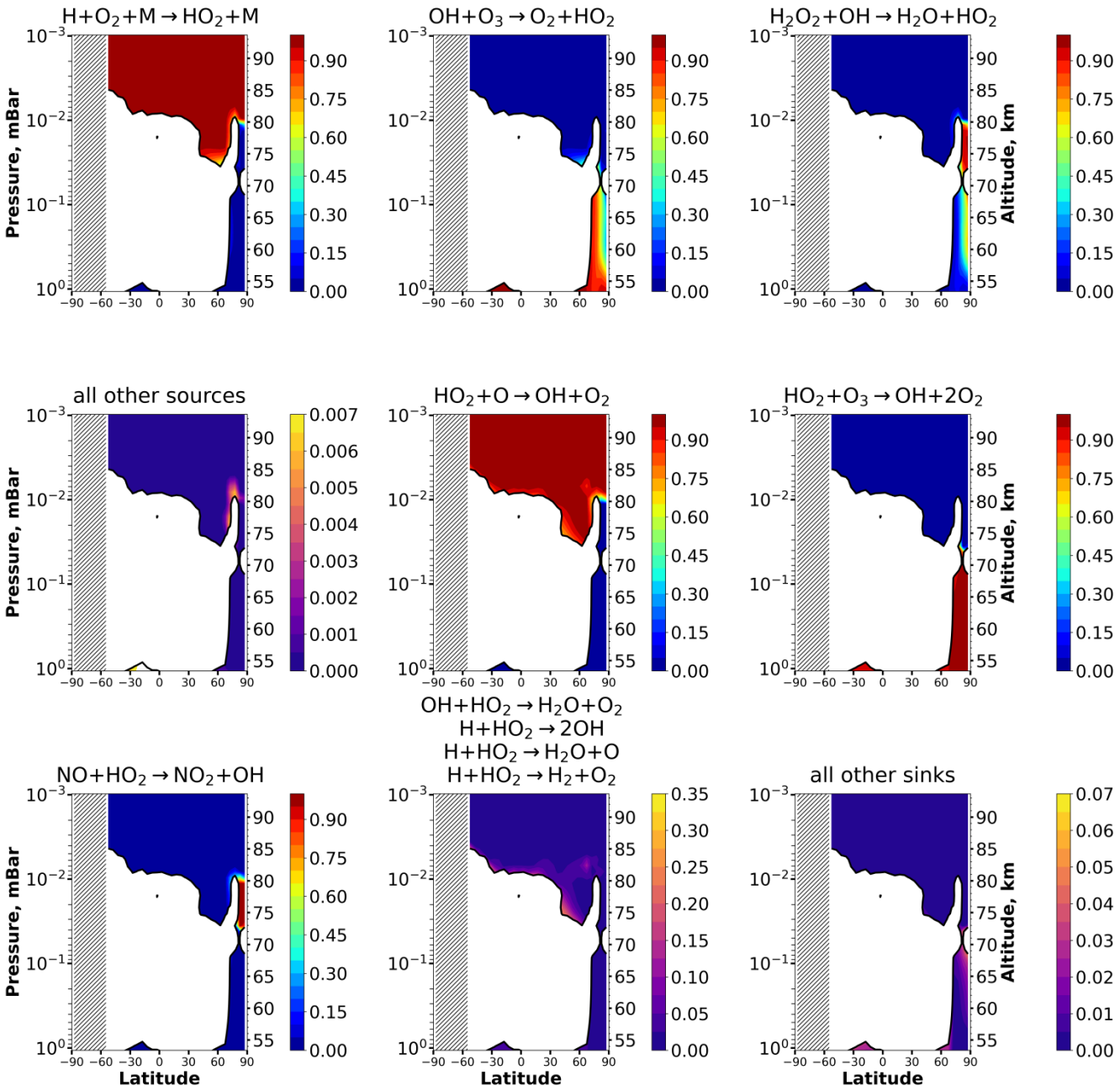
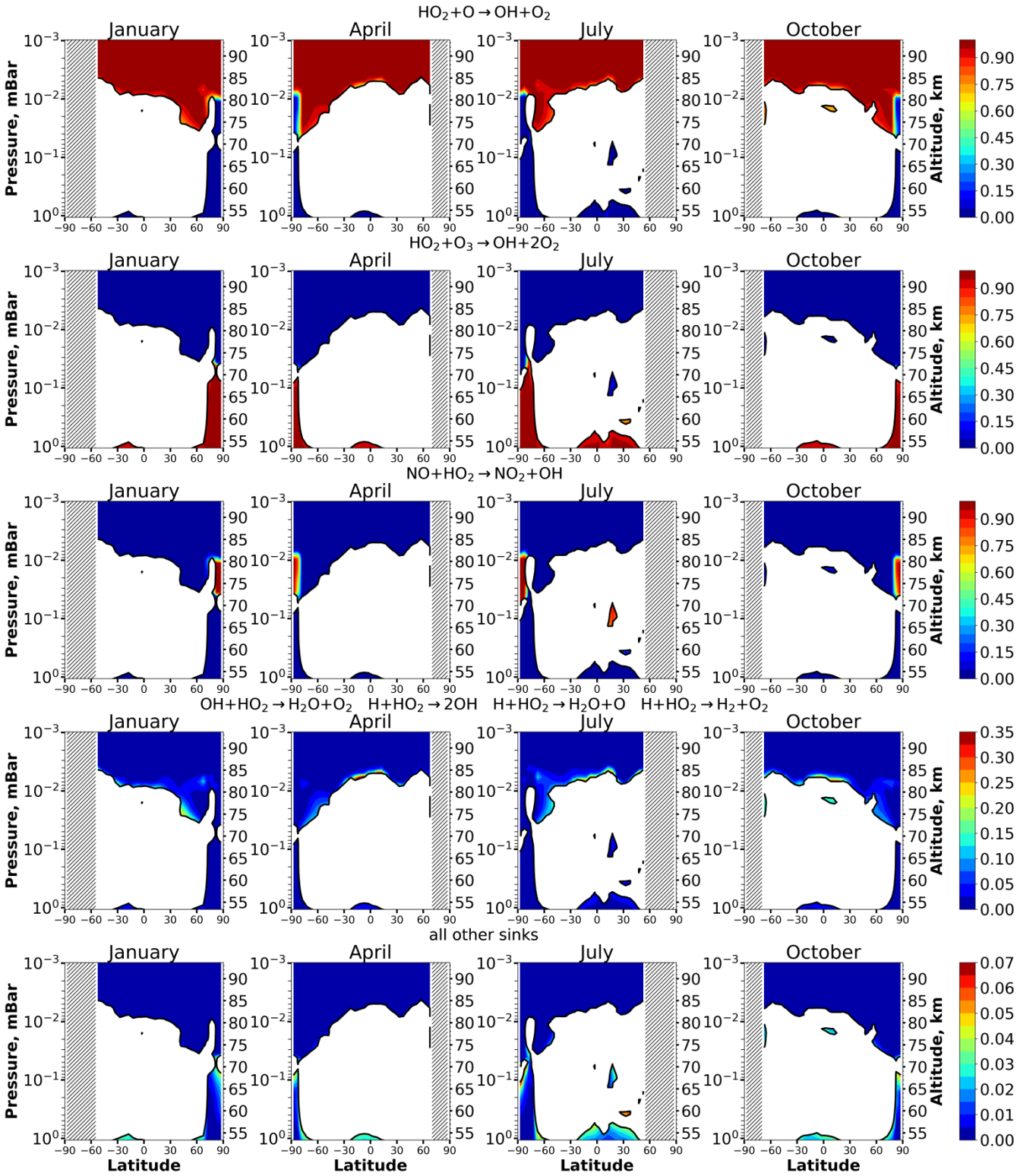


Figure 3. Nighttime mean and monthly averaged ~~the~~ relative contribution of a certain reaction to the total source or sink of HO_2 in equilibrium areas. The stippling corresponds to $\chi<105°$. White color ~~points~~indicates nonequilibrium areas of HO_2.


$HO_2+O \rightarrow OH+O_2$
January
April
July
October
Pressure, mBar
Altitude, km
$HO_2+O_3 \rightarrow OH+2O_2$
$NO+HO_2 \rightarrow NO_2+OH$
$OH+HO_2 \rightarrow H_2O+O_2$
$H+HO_2 \rightarrow 2OH$
$H+HO_2 \rightarrow H_2O+O$
$H+HO_2 \rightarrow H_2+O_2$
all other sinks
Latitude

809

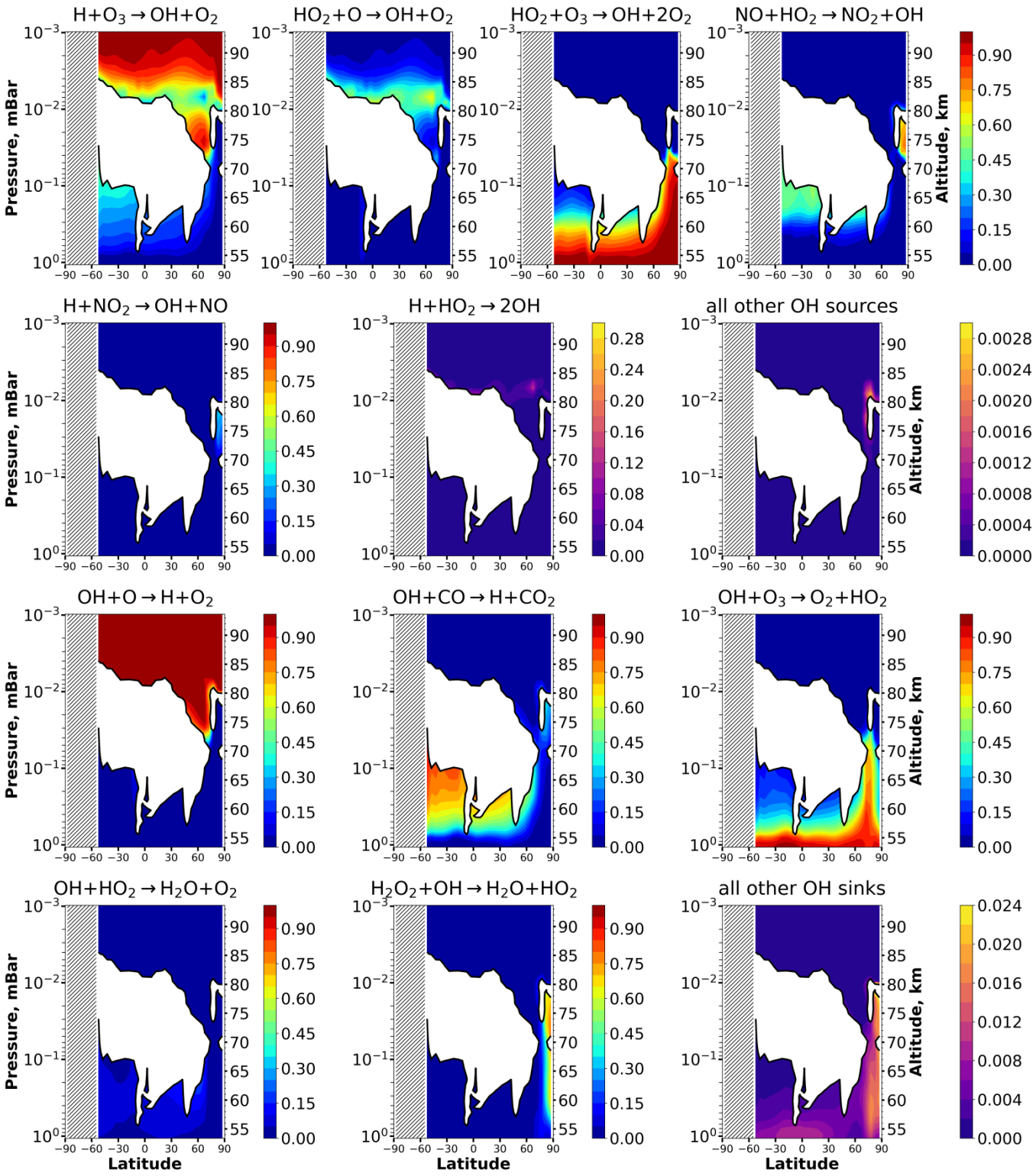
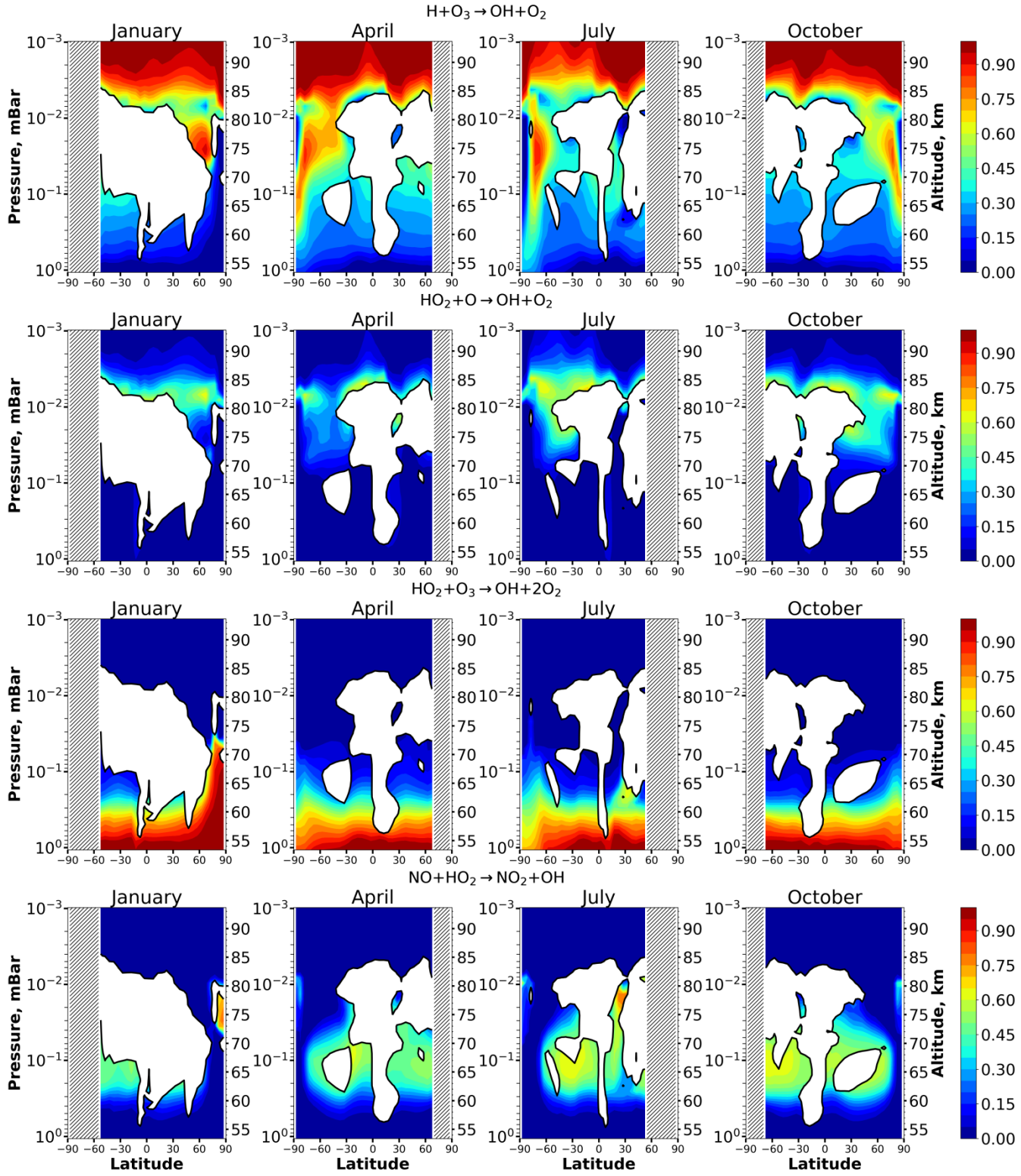
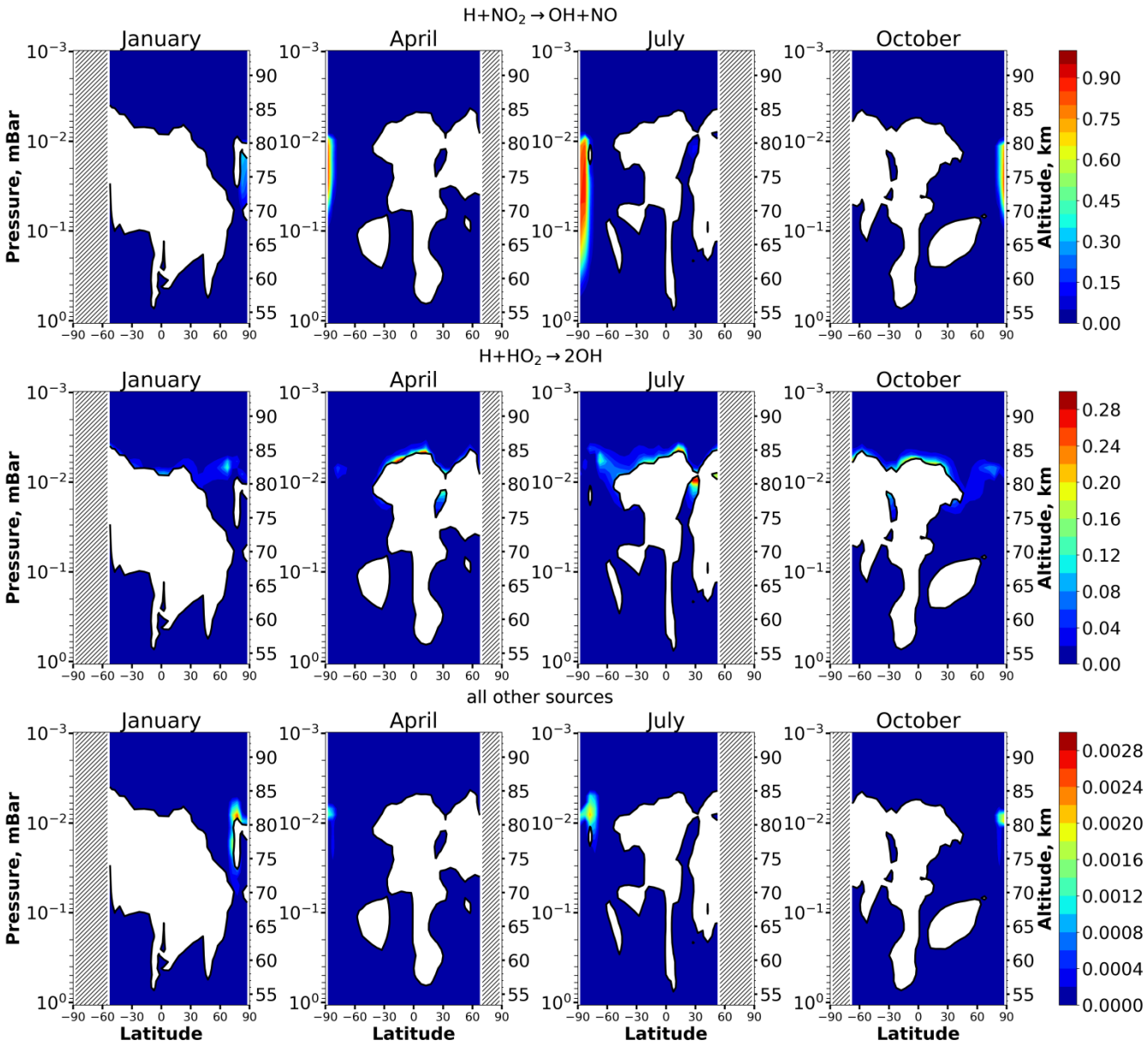


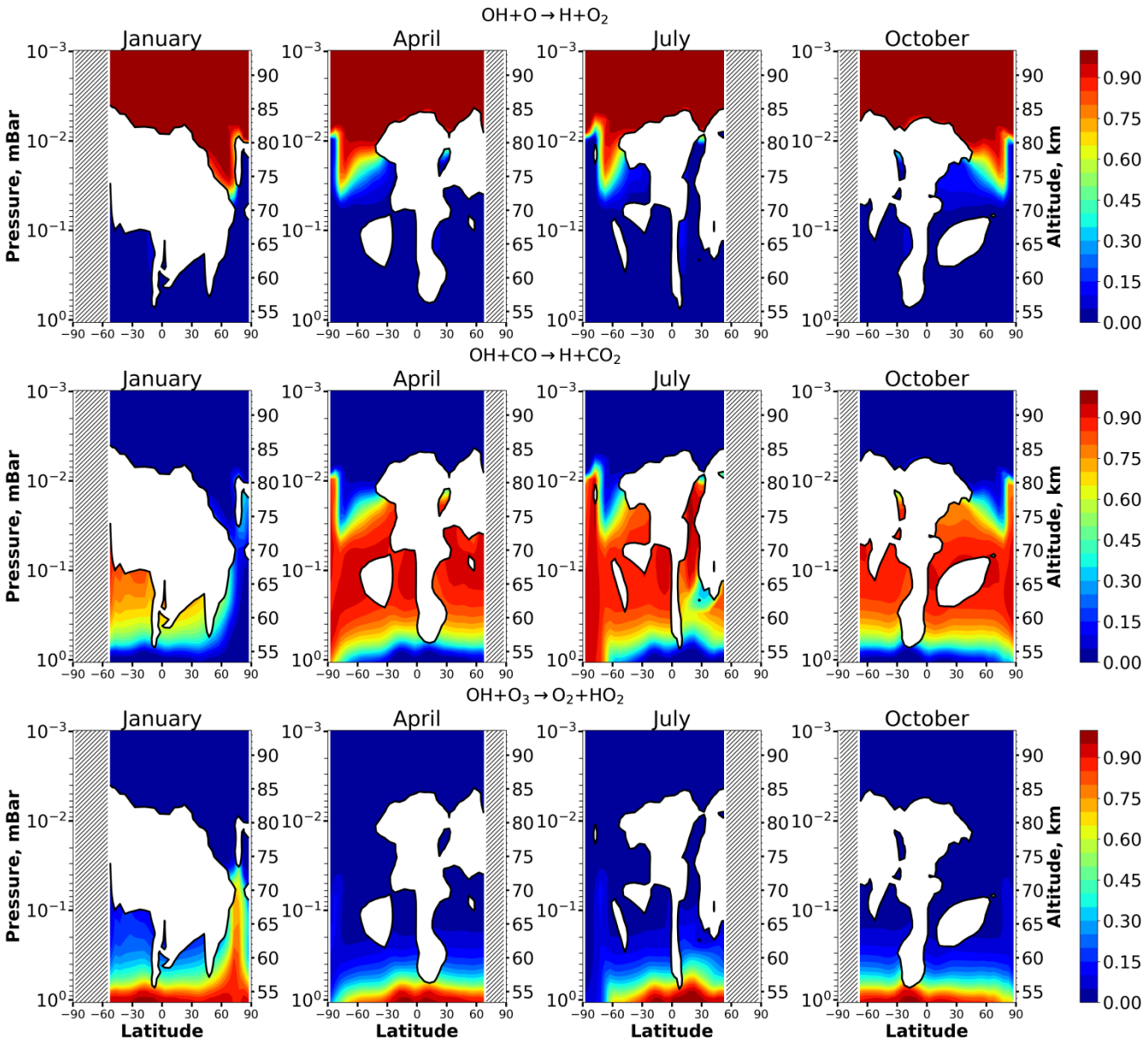
Figure 4. Nighttime mean and monthly averaged ~~the relative contribution of a certain reaction to the total sink of HO_2 in equilibrium areas. White color points nonequilibrium areas of HO_2.~~



~~Figure 5. Nighttime mean and monthly averaged the relative contribution of a certain reaction to the total source of OH in equilibrium areas (first part). White color points nonequilibrium areas of OH.~~



~~Figure 6. Nighttime mean and monthly averaged the~~ relative contribution of a certain reaction to the total source or sink of OH in equilibrium areas ~~(second part).~~. The stippling corresponds to $\chi<105°$. White color ~~points~~indicates nonequilibrium areas of OH.


OH+O → H+O2
January
April
July
October
Pressure, mBar
Altitude, km
OH+CO → H+CO2
OH+O3 → O2+HO2
Latitude

823

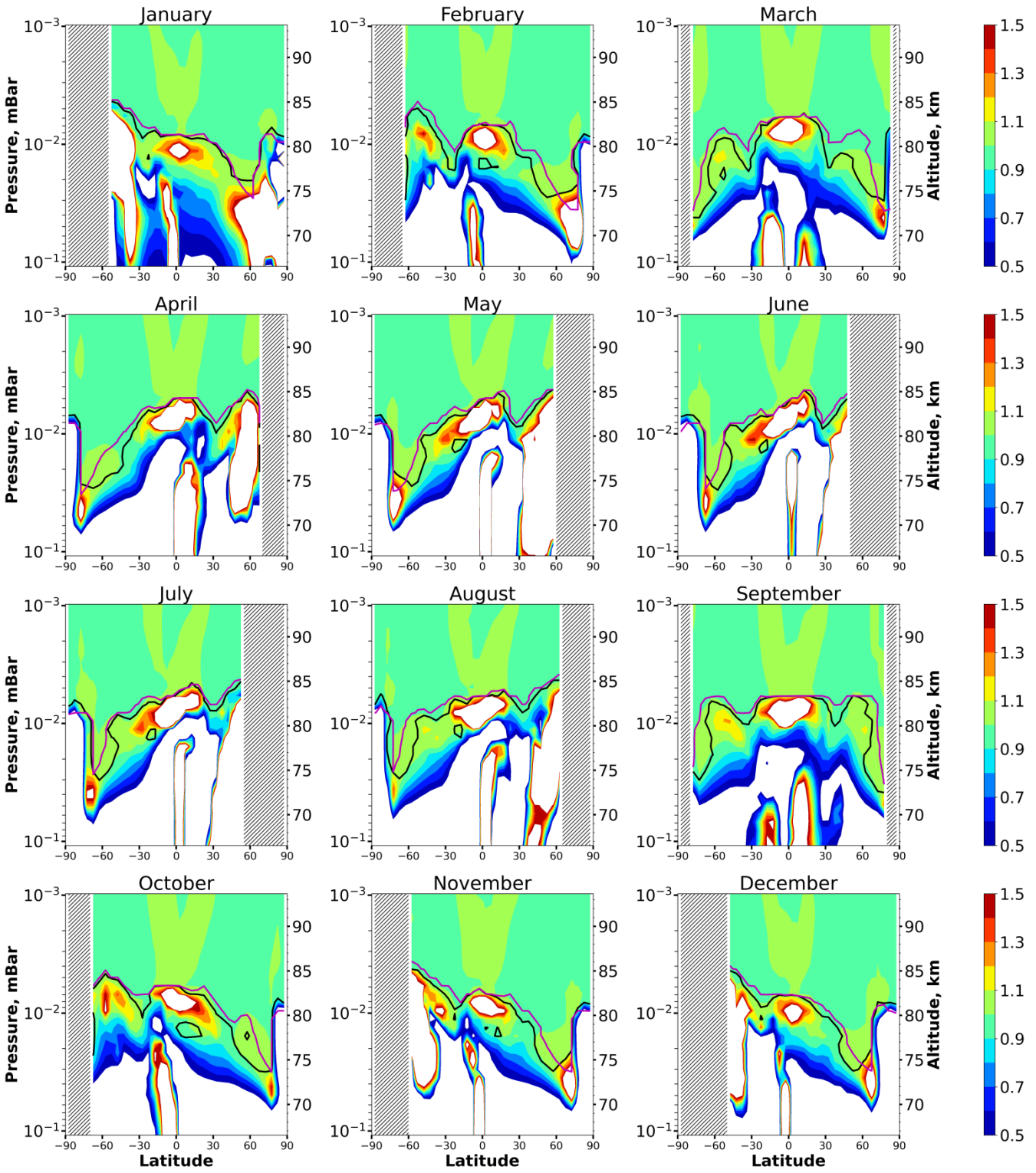


Figure ~~7~~5. Nighttime mean and monthly averaged ~~the relative contribution of a certain reaction to the total sink of OH in equilibrium areas (first part). White color points nonequilibrium areas of OH.~~

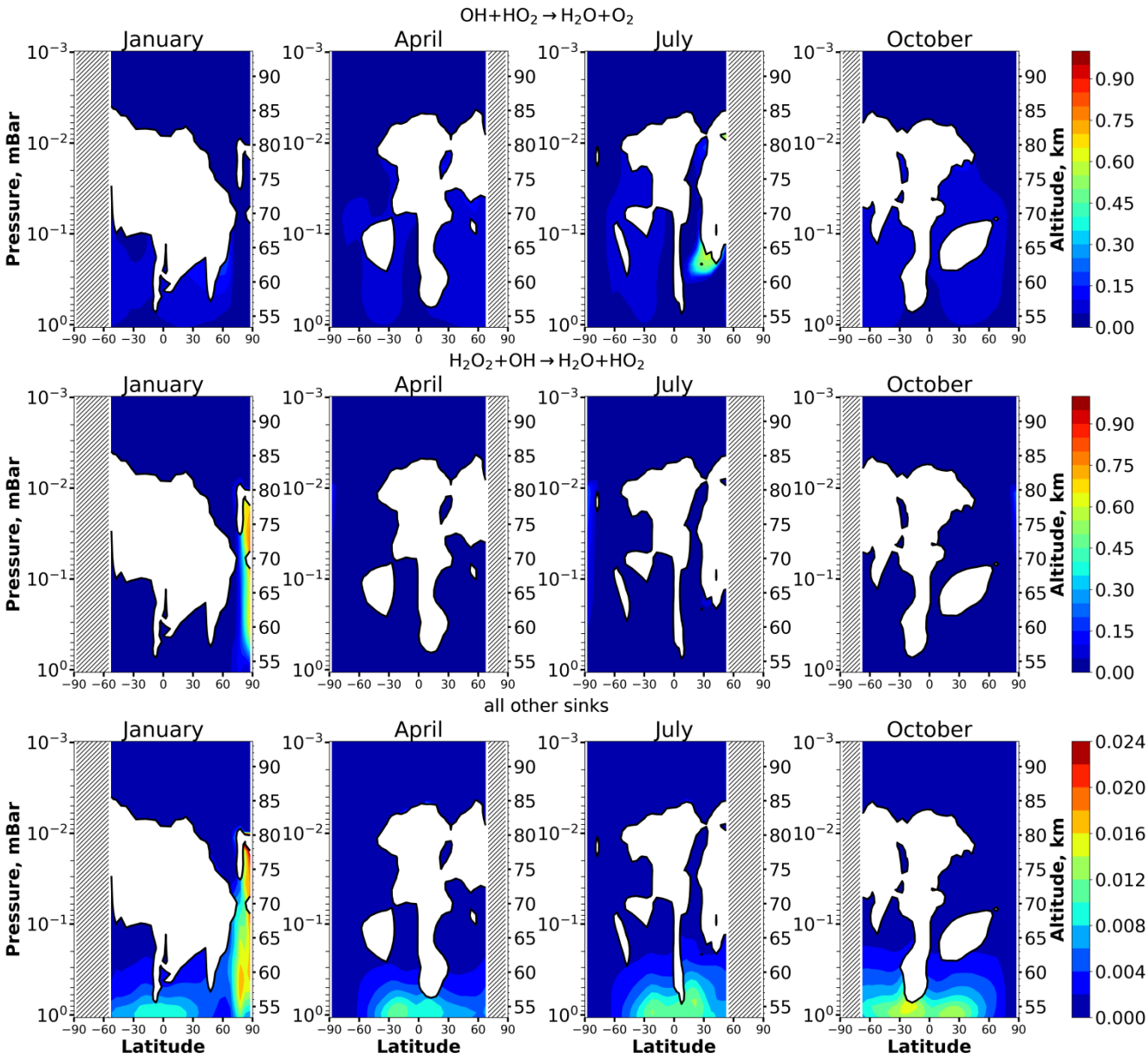
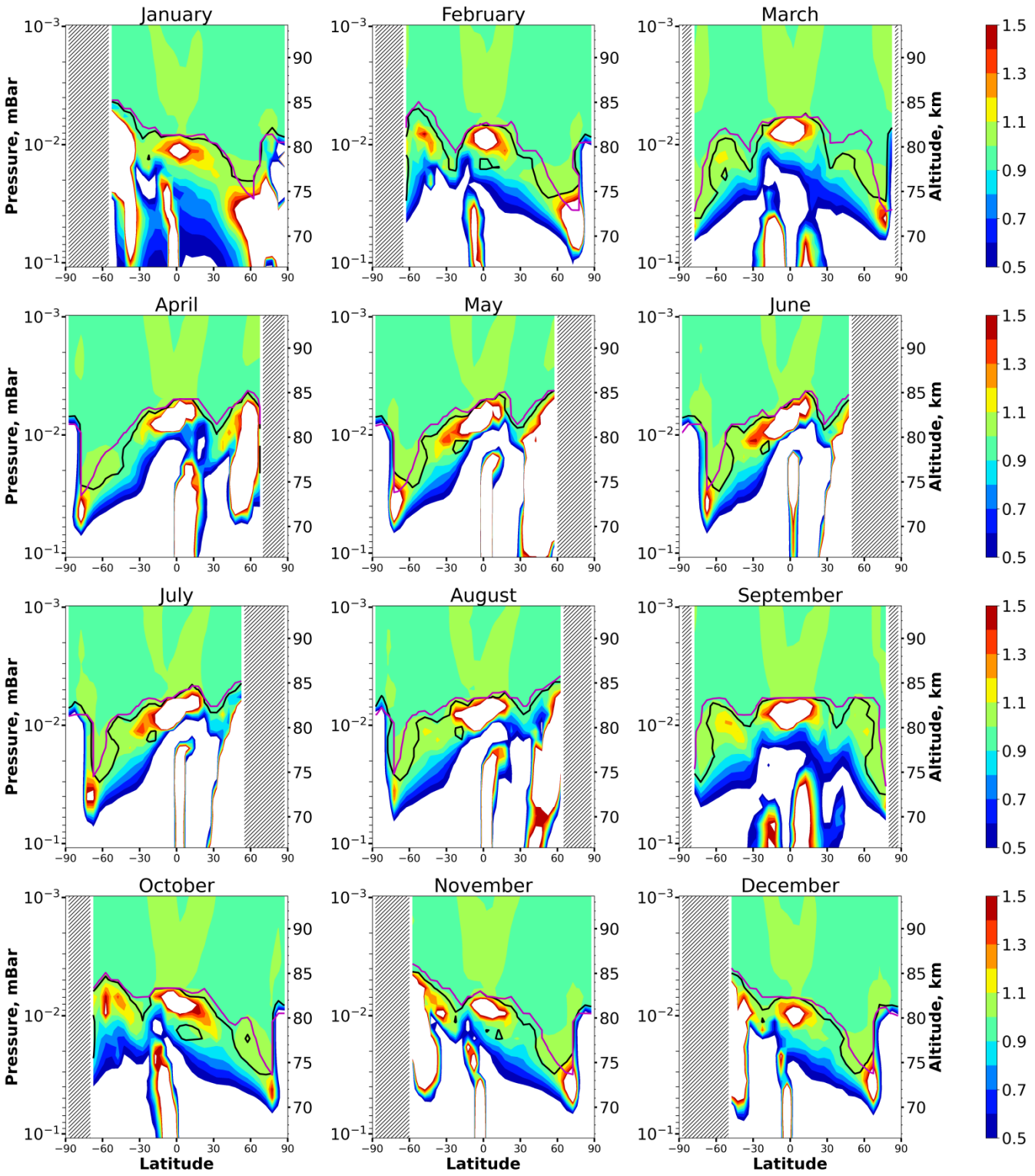
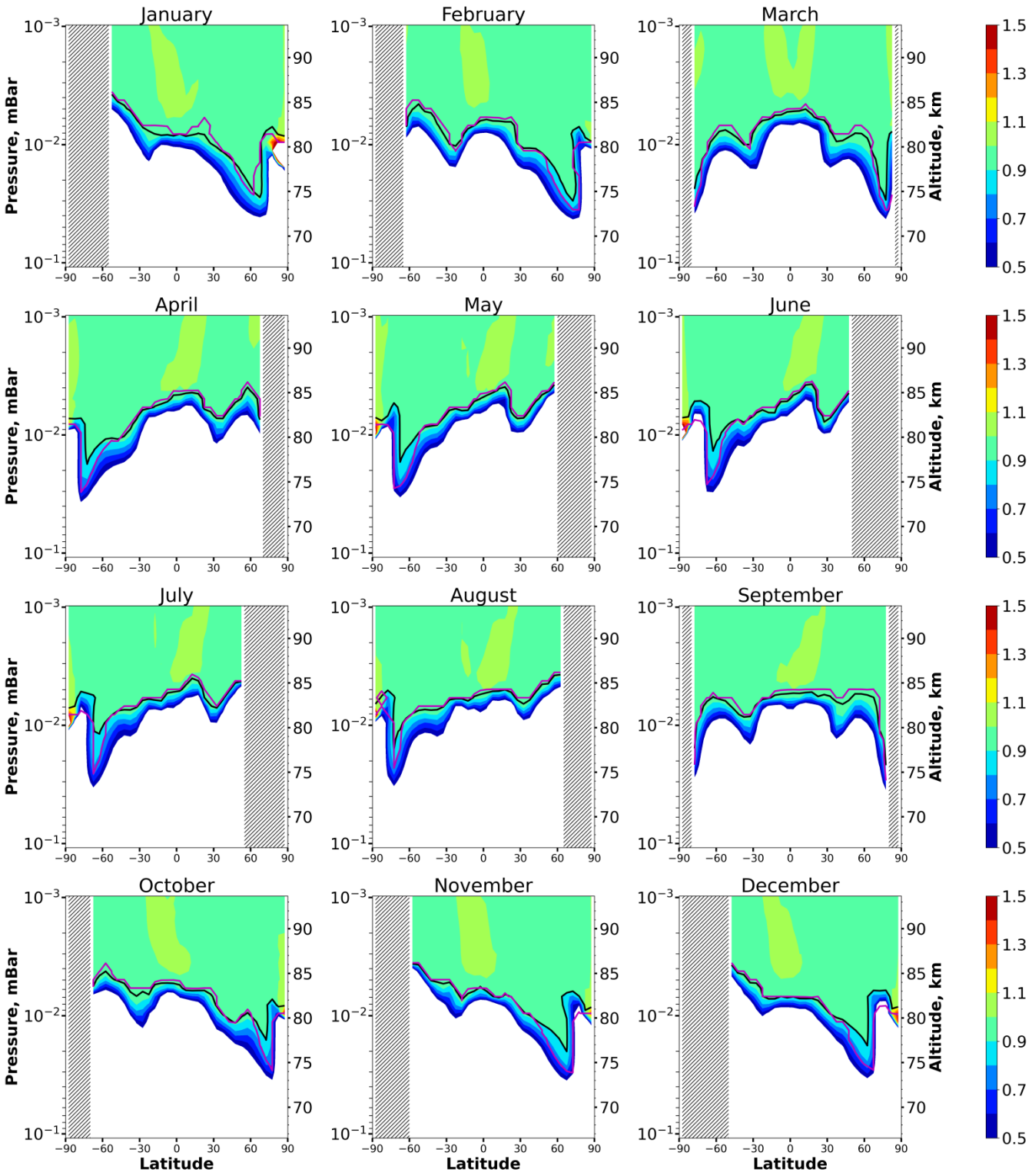


Figure 8. Nighttime mean and monthly averaged the relative contribution of a certain reaction to the total source of OH in equilibrium areas (second part). White color points nonequilibrium areas of OH.



~~Figure 9. Nighttime mean and monthly averaged~~ $HO_2/HO_{2_{sh}}^{eq}$~~.~~, where $HO_{2_{sh}}^{eq}$ is shortened equilibrium concentration determined by Eq. (9). Black line shows the ~~border~~boundary of HO_2 equilibrium according to condition (1). Magenta line shows $< Crit_{HO_2} >= 0.1$. The stippling corresponds to χ<105°. The white area represents the $< HO_2/HO_2^{eq} >$ ratio outside the [0.5, 1.5] interval.



839

840 ~~Figure~~

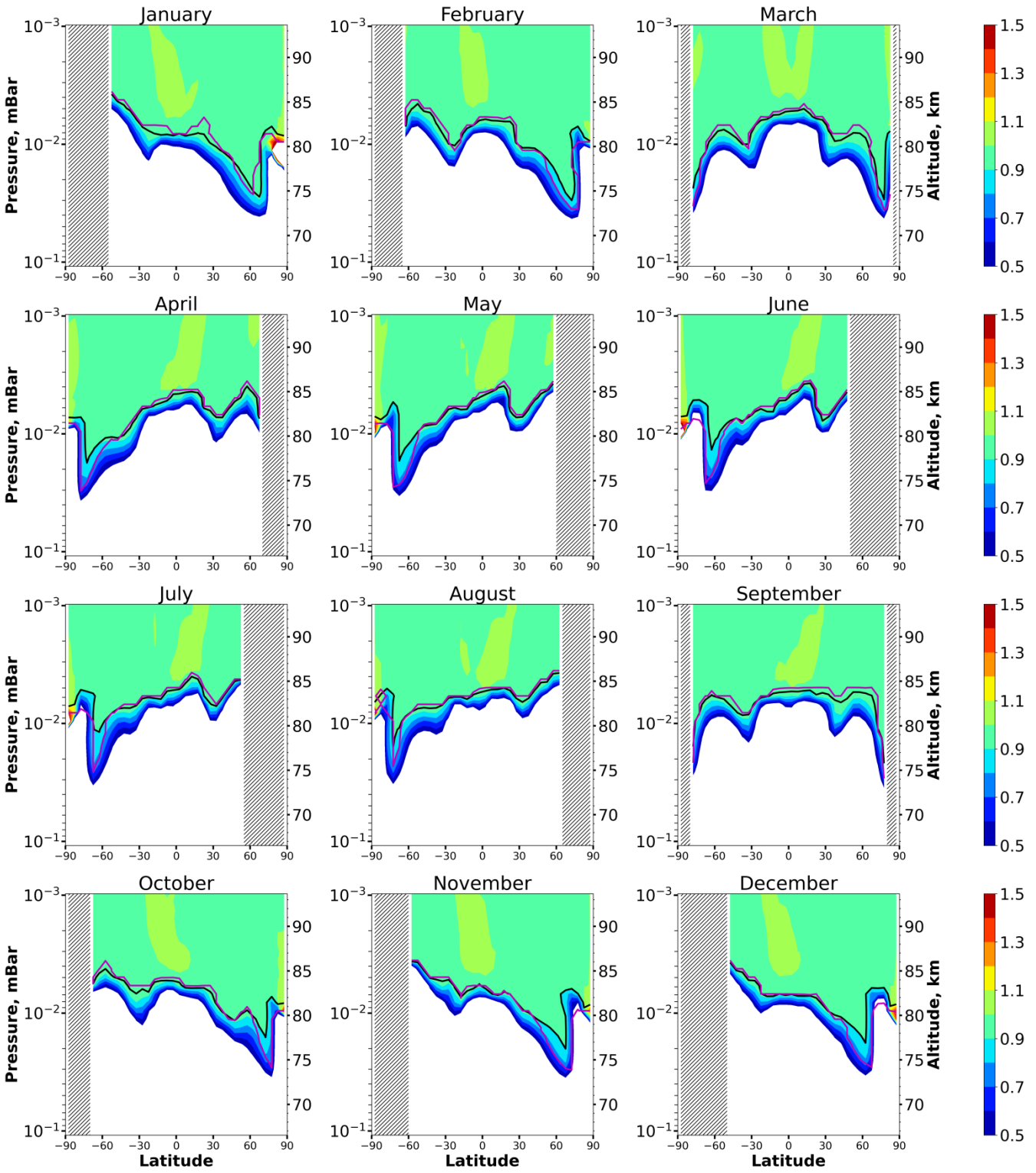
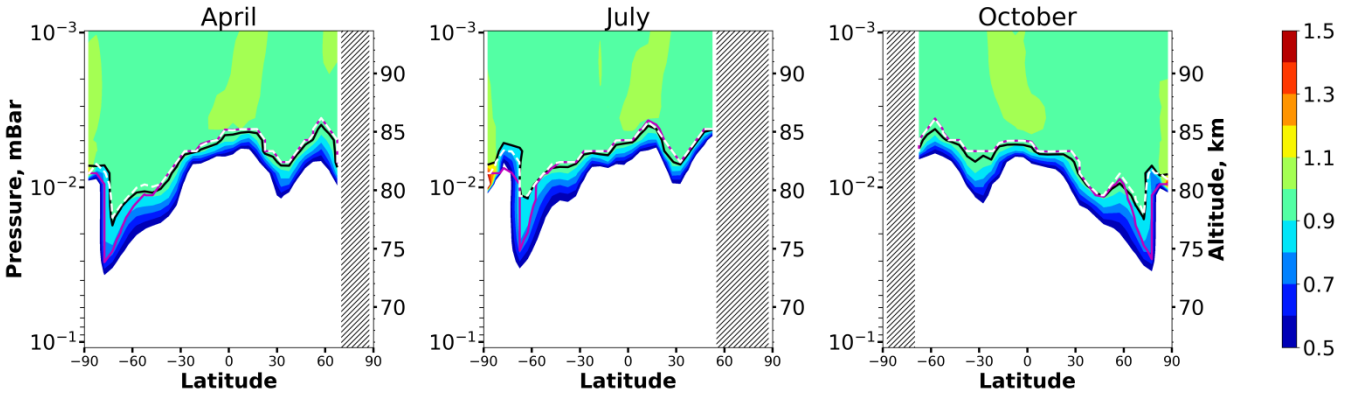


Figure 6. Nighttime mean and monthly averaged OH/OH_{sh}^{eq}, where OH_{sh}^{eq} is shortened equilibrium concentration determined by Eq. (10~~. Nighttime mean and monthly averaged OH/OH_{sh}^{eq}~~). Black line shows the ~~border~~boundary of OH equilibrium according to condition (1). Magenta line shows $< Crit_{OH} >= 0.1$. The stippling corresponds to χ<105°. The white area represents the $< OH/OH^{eq} >$ ratio outside the [0.5, 1.5] interval.


April
July
October
Pressure, mBar
Altitude, km
Latitude
Latitude
Latitude
10^{-3}
10^{-2}
10^{-1}
90
85
80
75
70
−90 −60 −30 0 30 60 90
1.5
1.3
1.1
0.9
0.7
0.5

847

848

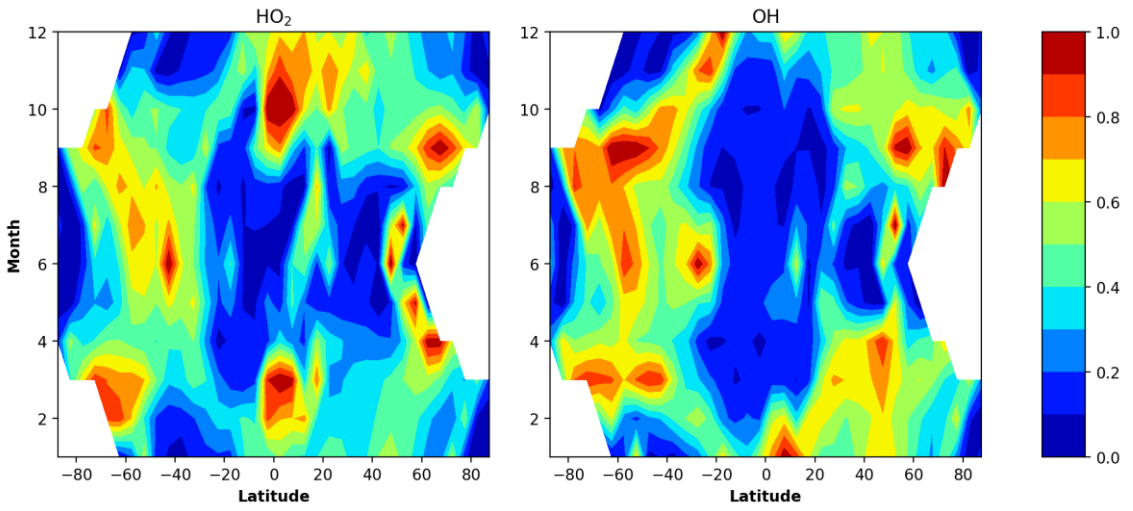


Figure ~~11~~7. Monthly and longitudinally mean of total uncertainties in determination of the local heights of the OH and HO_2 equilibrium boundaries according to the criteria (17) and (25). The white color indicates the absence of data due to polar day.

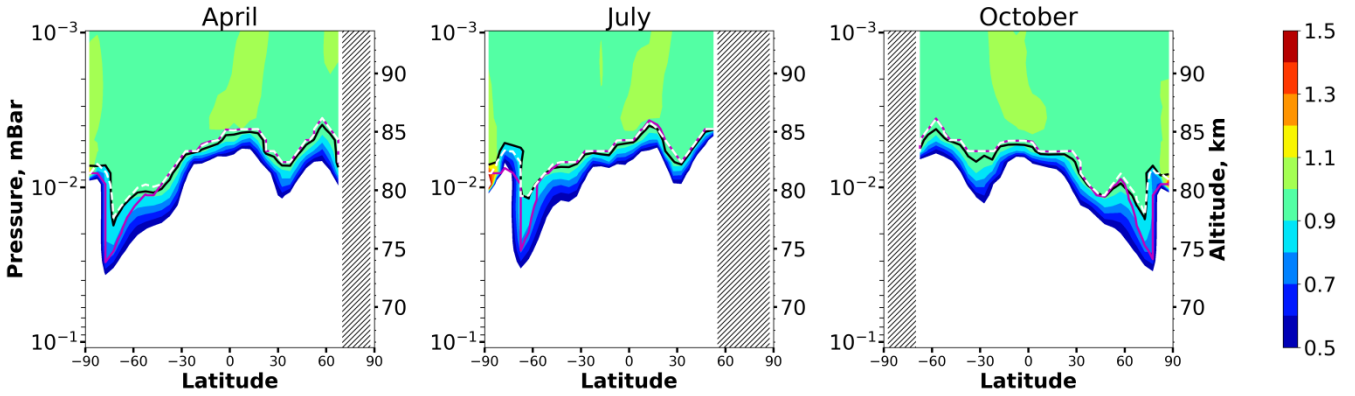
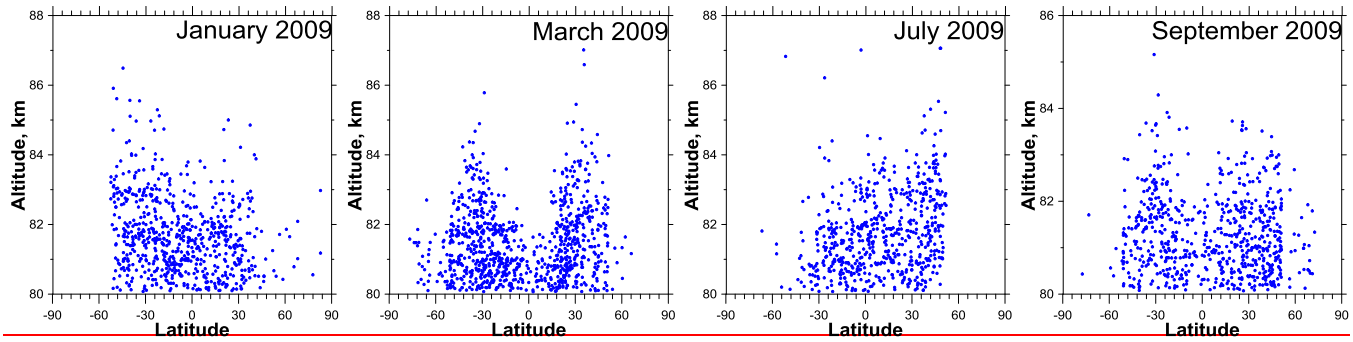


Figure 8. Nighttime mean and monthly averaged OH/OH_{sh}^{eq}. Black line shows the ~~border~~boundary of OH equilibrium according to condition (1). Magenta line shows $< Crit_{OH} >= 0.1$, dotted white line shows $< Crit_{OH}{}^{m} >= 0.1$.



~~The Figure 12. Blue dots point the found values of $z_{\partial H_{sh}^{eq}}$ above 80 km derived from the Panka et al. data in different months of 2009.~~