Review of "Boundary of nighttime ozone chemical equilibrium in the mesopause region: long2 term evolution from 20-year satellite observations" by Kulikov et al.

Overview

This paper presents a derivation of the nighttime ozone chemical equilibrium (NOCE) condition. The motivation for the paper is that minor atomic species O and H are key elements of the energy budget and chemistry of the mesopause region. These species have no readily/easily observable features to enable their direct observation by satellites or from the ground. Consequently, the approach used to derive these species is to infer them based on chemical relations between species such as ozone and observations of radiative emissions from the hydroxyl radical. The assumption behind these approaches is that ozone and the species H and O are in chemical equilibrium with each other at night.

The paper derives conditions under which the equilibrium assumptions would be true and assigns the upper altitude limit of these as the 'NOCE boundary.' The NOCE boundary is derived in depth based on observations made by the SABER instrument for the 20-plus year length of the mission. The NOCE boundary is analyzed in terms of altitude, latitude, and time. The NOCE boundaries are also examined for correlation with the 11-year solar cycle and for trends.

The paper presents interesting considerations for the derivation of O and H in the mesopause region from satellite observations. These considerations are important for the ongoing SABER instrument on the TIMED satellite and for analysis of data from the SCHIAMACHY instrument that formerly operated on EnviSAT.

Recommendation

The paper is returned for major revision. Below in the "Comments" section I list a number of comments for the authors to address. These are in no order of importance but rather they are chronological according to the paper.

There is one major weakness that I have for the entire paper – despite all the analyses of the NOCE boundary, and the apparent demonstration that ozone is not in chemical equilibrium over much of the mesopause region, the paper makes no statement as to how current the assumption of chemical equilibrium by SABER and SCHIAMCAHY affects the quality and the uncertainty in those datasets. Do they need reprocessing? How would that be done? What should current users assume for their analyses using these data? A revised paper must answer these questions.

Another major weakness in the paper is the trend analysis presented in Figures 12 and 20. These and their accompanying analyses and discussions must be deleted. The uncertainties (1-sigma) are larger than the derived trend, indicating that the trend is insignificant.

Also, the distinction between z_{eq} and z_{eq}^{pa} is not clear nor is the approach for deriving z_{eq}^{pa}. The paper needs to examine and clarify if these really are different parameters and why they both need to be analyzed to understand NOCE from a perspective of retrieving O and H from satellite observations.

The authors are also given several items in the Comments regarding the analysis and interpretation of the SABER data to address.

Comments
Line 40 – I believe the authors intend the word 'reach' instead of 'rich'.

Line 93-94 – It seems a word is missing between "according" and "the mentioned". Perhaps the authors mean "according to the mentioned"?

Line 120-124. The authors neglect loss of ozone by reaction with atomic oxygen in the mesopause region. At the level of which they appear to be investigating the chemistry, this process should be included. Table 1 confirms that this reaction is not considered.

Line 146-148. The authors need to specify which 'nighttime data' need to be 'excluded from consideration". O3, H, O, all?

Figures 1-3. The magenta line is very difficult to see in the figures unless they are substantially enlarged on the screen. It is also confusing with the large areas of similar colors above about 85 km in all figures. Perhaps a black line would be more visible? The caption should also state the meaning of the Cr = 0.1 condition/boundary to facilitate the interpretation of the figure.

Lines 170-185. The analysis here must be re-worked and compared with the model and derivation of O and H reported by Panka et al., including the results of H and OH reported in the literature. To date there has been no extensive comparison of the Panka et al. [O] results with the Mlynczak et al., 2018 results. The Panka et al. approach appears to more rigorously include the recent discovery of the importance of collisions with $O(^1D)$. The Panka data are hosted on the SABER website.

https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2018GL077677

https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2020GL091053

Line 191 – First full sentence, "In *the* second case.."

Line 194-198, and the subsequent description of Figures 4, 5, 6, and 7. The exact altitude of each pressure level is included in the SABER database. There is no need to approximate these altitudes based on a small subset of approximate altitudes and pressures mentioned in the Mlynczak 2013a and 2014 references. These altitudes are derived by SABER consistent with hydrostatic balance and the very accurate pointing of the SABER instrument. As presented in the paper, there could be substantial error in the assignment of altitude based on the method of altitude assignment as described by the authors.

Line 198. The authors should also specify, again to remind the reader, the meaning of p_{eq} and z_{eq}^{pa}, and state this in the Figure captions.

Figure 6. The comparisons shown are for calendar months. The paper mentions 'changes in satellite geometry'. These 'changes' are such that the local time sampled by the spacecraft (and

hence, by SABER) is does not remain constant in a given calendar month over the course of the mission. It is slowly drifting. Thus, the local times sampled in every "January" are not the same over the course of the mission. Please see:

https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2018JA025892

This fact suggests that the results in Figure 6 and any other Figure or results involving monthly calculations or comparisons may be incorrect.

Figure 7. Please mark the periods less than one year on the x-axis to make it easier for the reader to discern these. What is the statistical significance of these features? Have the authors considered a Lomb periodogram which provides a significance test for the derived periodic features?

Lines 234-243. The paper describes anticorrelation between average z_{eq}^{pa} and the 11-year solar cycle. The authors should provide some rationale for why the altitude/pressure at which night ozone is (or is not) in photochemical equilibrium depends on the slowly varying solar cycle. Specifically, what atmospheric characteristics cause this? Is it a feedback from temperature and perhaps the 'breathing' or expansion and contraction of the atmosphere with the cyclic heating and cooling of the solar cycle?

Line 244-249. It is assumed that the uncertainties plotted in Figure 12 are 1-sigma values. All of the 1-sigma uncertainties are larger than the derived trend value, except at 20 N. At 2-sigma, all of them are. These results and figure 11 should be removed from the paper as the significance of them is marginal at best.

Figure 13. The color bar is very difficult to read as the altitudes all run together. It is also very difficult to discern anything quantitative about the annual variations shown in the figure.

Figure 14. Although there are differences in Figures 5 and 14 (z_{eq}^{pa} and z^{eq}, respectively), it is not clear what these differences are trying to show, or if there is a real difference. See my previous comment about the assignment of altitude to z_{eq}^{pa}. For clarity, SABER's natural vertical coordinate is pressure. All the data are retrieved as a function of pressure. There is no 'assignment' of pressure. Similarly, the temperature retrieval profile that is in hydrostatic equilibrium, the altitudes assigned to the pressure surfaces are accurate, and are derived in part from the accurate knowledge of the position of the field of view of the instrument as is scans the limb.

Figures 17-18. Same comment as for Figure 14.
Figure 19 and 20. These results and Figures should be deleted. The trends in Figure 20 are not significant even at the 1-sigma level.

Line 290-297. The reason for the discrepancy noted in the z_{eq} and z_{eq}^{pa} may have a simple explanation, as noted above. It is not clear how the authors assigned z_{eq}^{pa}, as noted above.