

Interactive comment on “Technical Note: Evaluation of simultaneous measurements of mesospheric OH, HO₂, and O₃ under photochemical equilibrium assumption: Statistical approach” by Mikhail Yu. Kulikov et al.

Anonymous Referee #2

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I recommend the paper for publication in ACP after some minor corrections and changes. The concentrations of three constituents, OH, HO₂, O₃, have been measured by satellite and additionally calculated by a 3D global chemical transport model. The authors used MLS/Aura data in their paper inserting the measured concentrations into a derived formula. They apply a sophisticated statistic Bayesian validation technique. Likewise the concentrations of the same constituents have been calculated on the basis of the chemical transport model LIMA. The authors compared the results of both measurements and calculations and discuss the differences between them. In my

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opinion a surprising result is that the derived expression does not explicitly depend on water vapor, but implicitly it depends on water vapor by the concentrations of the acting species.

In case of photochemical equilibrium, known temperature and pressure profile 5 nonlinear algebraic equations determine the concentration of the chemical active species H, O, OH, OH₂, and O₃ in the MLT-region. Atomic oxygen and atomic hydrogen are the main active chemical constituents in this system. A further assumption in this study is that transports also can be neglected. The system depends then, in essential, on the variable concentration of water vapor. On condition that also the temperature-depending reaction rates and the dissociation rates are known, one could theoretically derive, if the concentration of only one constituent was measured, the concentration of water vapor or any other constituent.

Photochemical equilibrium occurs in the MLT-region only during daytime. If more than one constituent were measured one has the opportunity to check model calculations or to inspect the agreement to observed data. On the one hand the authors use for analysis in their paper satellite measured concentrations of OH, HO₂ and O₃. Neglecting the small term $JH_2O[H_2O]$ in the equation for OH (equation 10) both main chemical active constituents, O and H, can stepwise be eliminated from the system (first O in equation 13), and an expression of the structure $F(OH, HO_2, O_3)=1$ can be derived only depending on the measured constituents. This equation depends in nonlinear way on OH, HO₂ and O₃.

On the one hand the authors use model results of 3D-calculations and on the other hand they employ measured concentrations of these species. Deviations from unity are a hint to non-equilibrium conditions or to other reasons such as incorrect reaction rates, erroneous model calculations or errors in the retrieved data. The fundamental idea was to derive such expression not depending on water vapor. The interpretation of deviations from unity is certainly complicated. What means for instance -1% deviation or $F(OH, HO_2, O_3)=0.99$? It indicates that, generally speaking, the agreement is quite

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good. But in case of stronger deviations it is difficult to say, what is the reason for this discrepancy? Minor comments:

The paper has a very voluminous introduction of about 39% related to the entire paper. It has the character of a review paper. I will not criticize that, but I will only mention here.

Line 165: 150 km is already the middle thermosphere.

Line 174: entered, maybe better mentioned

Line 178: $H=7$ km is an approximated mean scale height. (1 km scale height corresponds to about 33 K or 7 km to 231 K mean temperature)

Line 194: reaction rate constants; according to? Quotation?

Line 198: The net production term of hydrogen radicals is in essential $JH_2O[H_2O]$. Why do you neglect this term in (10)? Too small compared with the other terms in equation (10) and consequently the approach do not depend on water vapor?

Line 202: ...of ozone ()?

Line 204: The aim is to eliminate O and H and to derive an expression only depending on OH, HO₂, O₃.

Line 211: $\alpha=(...)$ could be equation (14.2) and (14) then (14.1) or (15) and the following equations (x+1).

There is a large step from equation (10) – (13) to equation (14). Could you give some intermediate steps?

Line 218: k_2 decreases strongly below the lower mesosphere and stratopause. Ozone is no longer in photochemical equilibrium there.

Line 234: ...certain altitude z...

Line: 239: Factor $\sigma_j \sqrt{2 \pi}$?

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Line 296: ...fall into one...

Line 304-318: In the lower thermosphere the system is not in chemical equilibrium. Transports play a significant role (see also Grygalashvyly et al. 2012).

Section 6: The characteristic time of atomic oxygen is about $\tau_O=(k_1O_2M)^{-1}$. At 90 km is $O_2=1.47 \times 10^{13}$ cm⁻³, $M=7 \times 10^{13}$ cm⁻³, and $k_1 \approx 10^{-33}$ cm⁶s⁻¹ depending on temperature. The characteristic time has then an order of 106 s. About one order smaller is the characteristic time of H, but still large. Both the production and the loss term of HO₂ depend on H and O being not in photochemical equilibrium in the lower thermosphere. Therefore a discrepancy relating to HO₂ one should expect.

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