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Interactive comment on “Retrieving the vertical distribution of stratospheric OClO from Odin/OSIRIS limb-scattered sunlight measurements” *by* P. Krecl et al.

Anonymous Referee #1

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General comments:

The paper presents an important scientific material which can be of great importance for the atmospheric science. However, the presentation quality is rather poor. The paper is too much similar to the previous paper of the OSIRIS group [Haley et al., 2004] and contain a lot of material already discussed there rewritten in other words. The discussion of method and results is not always clear and concise. Some of the statements in the “Comparison” and “Results and conclusions” sections are poor substantiated or misleading. Some references are inappropriate. In general, the paper is suitable to be published in ACP after a major revision including a reconsideration of the presentation form and clearing important issues listed in the detailed comments.

Specific comments:

1. Nearly the entire Section 3.1 is unnecessary because the basis of the DOAS method is widely known and sufficiently discussed in the recent papers. Moreover, the DOAS spectral analysis as applied to OSIRIS measurements was previously discussed in [Haley et al., 2004] using the same formulas. The first part of the section should be removed.

2. Page 2994, line 18: "Note that in the limb viewing geometry, I_o represents a scattered solar spectrum free from molecular absorption and Rayleigh and Mie extinctions."

I_o can be an extraterrestrial solar spectrum of any kind. It does not necessary need to be a scattered spectrum. The sentence has to be rewritten.

3. End of Section 3.1: The chi-squared statistics is only meaningful if the real measurement noise can be estimated. Thus, some comments on how to estimate the measurement noise of the OSIRIS instrument are required.

4. Section 3.2: "The spectral structure of OClO, shown in Fig. 2, suggests that the differential absorption spectroscopy ...."

It is very difficult to suggest anything about differential method analyzing the absolute cross sections. In order to be able to analyze possible cross-correlations, the differential cross sections need to be plotted. It is even better to plot this cross sections multiplied by typical slant columns to see the relative amplitudes of spectral signals associated to different atmospheric species absorbing in the selected spectral range.

5. Section 3.2, page 2998, Fig. 4: It would be interesting to see both OClO spectral fits and residuals. The shaded region is difficult to see in the printed version.

6. Section 3.2, page 2998, line 16: "A significant cross correlation between OClO and

BrO absorption cross sections for wavelengths shorter then 380 nm could, to some extent, explain the larger residual structures..."

This is pretty unbelievable. How can a correlation between cross sections increase the fit residual? Although, as you said, it could be a reason of the large difference in ECD. More realistic would be a smaller residual and wrong ECD values, wouldn't it?

7. Section 3.2, page 2998, line 22: "This is consistent with the negative OClO abundances observed by other authors" is a very funny statement. Are you pretending to see impossible as good as other authors do? If you think your negative values could be real you have to find a physical explanation of this effect, e.g., larger OClO abundances in higher altitude layers. Otherwise, if you think that the OClO concentration was too low resulting in the loss of the sensitivity of the measurements you have to classify this ECDs as undetectable. In this case you can only state that other authors did not detect any significant OClO amount under similar conditions. Concluding, it is wrong to say that a value which you do not trust is in agreement with any other measurements.

8. Section 3.3: The nature of all spectral corrections was already discussed in [Haley et al., 2004] and does not need to be discussed again. It would be enough here to discuss the issues specific for OClO, e.g., the impact of the correction appliance on the retrieved ECDs.

9. Section 3.3, line 11: Some comments on how to obtain the relative ECD error are required.

10. Section 3.3: The method to decide if a spectral correction is applied or not is doubtful. A spectral correction which systematically reduces the residual and changes the ECDs is always treated as useful, although it only means that the correction correlates to some extent with the OClO cross section. Under certain conditions such a spectral correction can deteriorate the retrieved ECDs even if it is reducing the residual. Such method can be used without any dispute to analyze the corrections which are not involved into the LSQ fit such as solar I_o effect or wavelength shift. For spectral

ACPD
5, S1037–S1048, 2005

Interactive Comment

EGU

corrections included in the least-square fit the suggested method is only suitable to select out corrections which have almost no effect such as the polarization correction. An additional control method could be to analyze the reasonability of the fit coefficients of the spectral corrections, i.e., if they have correct signs, expected amplitudes and tangent height behavior.

11. Section 3.3.3: The fact that the Ring effect correction mostly impairs the spectral fit can be an indication of an inappropriate modeling of the Ring effect.

12. Section 3.3.4: It would be more interesting to show the polarization parameter after the subtraction of the second order polynomial, i.e., the remaining spectral structure which is used as a pseudoabsorber in the differential LSQ fit.

13. Section 3.3.5: The formula for the tilt correction appears without any explanation with a reference to [Haley et al., 2004] where no comments concerning the origin of the formula can be found as well. In both papers the work of [Sioris et al., 2003] cited as a motivation to use the tilt correction as a pseudoabsorber in the LSQ fit. Leafing through the cited paper one obtains from the description in the Section 2.1.9 a little bit different formula for the tilt correction:

$$t(\lambda, h_t) = \frac{I^{os}(\lambda, h_t)}{I^{os}(\lambda, h_{ref})} - \{second\, order\, polynomial\} \qquad (1)$$

where $I^{os}(\lambda, h_t)$ and $I^{os}(\lambda, h_{ref})$ denote the spectral radiances at a low and high tangent height, respectively, which are obtained calculating highly resolved and sampled spectra and then convolving and binning them according to the OSIRIS pixel-to-wavelength mapping and spectral resolution.

At this point you have either to prove that your formula results in the same structure of the tilt pseudoabsorber as proposed in [Sioris et al., 2003] or to remove the reference to this paper and suggest your own motivation of the employed formula for the tilt correction.

ACPD

5, S1037–S1048, 2005

14. Section 3.3.5, calculation of the tilt pseudoabsorber: The proof that the tilt effect can be used as a pseudoabsorber in the DOAS LSQ fit presented in [Haley et al., 2004] (Eq. (21) in Section 3.2.5) is based on the assumption that the spectral structure of the tilt contribution is independent from the tangent height below the reference. Thus, according to this approach there is absolutely no need to calculate the tilt pseudoabsorber for different tangent heights. If authors pretend to be more accurate using a modified approach they should use the same reference as in the measured spectra, i.e., the average of limb scattered spectra between 40 and 70 km (page 2994, lines 22 – 24) rather than a spectrum at 50 km tangent height.

15. Section 3.3.6: A possible shift of the reference spectrum with respect to the spectrum at the current tangent height can have much larger effect compared to the shift of the measured limb-scattered radiance with respect to the absorption cross sections. Thus, a complete investigation of the wavelength shift impact should include an investigation of a possible misalignment in the wavelength calibration of the individual limb spectra with respect to the reference measurement.

16. Section 3.3.7: According to Section 3 only the differential component of the optical depth is considered. Thus, one can expect that both observed and fitted optical depths have to be varying around the zero level, i.e., they have to show both negative and positive values. Why is this not the case in Fig. 7?

17. Section 3.4: “Additionally, since absorption is a linear process only for optically thin conditions, the problem becomes non-linear in the UV/blue region where the high Rayleigh scattering efficiency could lead to large optical depths at low tangent heights.”

Here, authors fail to distinguish between different kinds of non-linearities which can arise in such kind of inversion problems. Authors seem to discuss the non-linearity resulting from the increased absorption by the atmospheric species of interest caused by the increased mean photon path lengths due to strong Rayleigh scattering. This non-linearity resulting in the limitation of the validity of the ECD approach is related to the current state of the atmosphere only and can not be avoided in any iteration process. Another non-linearity can arise from the replacement of F by Kn, i.e., from the linearization of the forward model. If the true atmospheric state is too far from the initial state of the model it is possible that due to this non-linearity the "linear" solution will not coincide with the true state. This kind of non-linearity can be eliminated employing an iterative approach.

Authors have to clarify what they want to say writing this sentence.

18. Page 3007, line 3 – 5: Authors claim here to retrieve the natural logarithm of the concentrations. However, all the discussion below relates to the concentrations themselves.

19. Section 3.4.1: First part of the section is identical to the discussion in [Haley et al., 2004]. It should be removed.

20. Section 3.4.2: It is not clear if ρ values relate to the concentrations or to the logarithm of concentrations. Is $\rho = 3$ or $\rho = 3 \times n$ or $\rho = 3 \times \ln n$ or something else?

21. Section 3.4.3: Are the weighting functions for the concentrations or for the logarithm of concentrations discussed in this section? Please clarify it in the text.

22. Section 3.4.3: "The relationship between the derivatives of the RTM and the derivatives of F is not obvious because of the intermediate DOAS step."

Please clarify what you mean as " the derivatives of the RTM".

23. Section 3.4.3: "The first approximation is to reduce the number of spectral elements by using a two-wavelength DOAS approach as proposed by Haley et al. (2004)."

According to [Haley et al., 2004] this simplification is only applicable when no other species are interfering significantly with the target species at the two selected wavelengths. Authors are requested to demonstrated that for the selected wavelengths this requirement is complied with.

ACPD
5, S1037–S1048, 2005

24. Section 3.4.4: This section just reproduces the discussion presented in [Haley et al., 2004]. It should be removed.

25. Section 3.4.5: "This example is generally representative of the entire set of Antarctic OClO data measured on 19 – 20 September 2002."

This result has absolutely nothing to do with the measurements. It is only representative for a certain set of model initialization parameters and a priori information. Comparing Figs. 9 and 10 it is clearly seen that the altitude behavior of the response function is nearly the same as of a priori OClO profile. Apparently, this behavior is forced by a priori covariance matrix S_a containing the percentage concentration squares (if ρ is defined as $3 \times n$). Thus, for any other a priori OClO profile a different vertical behavior of the response function can be expected. Furthermore, as seen from Fig. 10 a priori information is chosen inappropriate. Thereby, the response function for the whole dataset can be affected resulting in the loss of sensitivity above 18 km.

26. Section 4, Fig. 10: According to Section 3.4.2 the OClO profiles simulated by the REPROBUS model were used as a priori information. Thus, both black and blue curves in Fig. 10 are supposed to represent the best collocated OClO profile simulated with the REPROBUS model. Please explain the difference between these two REPROBUS profiles and comment why the profile represented by the black curve was used as a priori rather than that given by the blue curve.

27. Section 4, page 3015: "... with a difference between peak values of less than 3%."

This statement is absolutely meaningless taking into account that the accuracy of the retrieved OClO concentration at 16 km is about 50%.

28. Section 4, Table 8: "The altitude of the OClO peak value and the shape of the profiles (not shown) are similar..."

This statement is somewhere between misleading and wrong. For example, profiles presented in [Pommereau et al., 1994] are peaking at 20 – 22 km and then decreasing

ACPD

5, S1037–S1048, 2005

Interactive Comment

quite rapidly with the altitude. Sure, in a certain sense they are similar to almost constant values between 14 and 18 km and almost no OClO at 20 km as obtained from OS measurements but this similarity is not strong enough to be just stated without presenting both profiles and making some comments. Actually, the only conclusion which can be drawn comparing these profiles is that they are different. And the explanation of the difference is also clear, the profiles were obtained in different hemispheres with an interval of 10 years. Thus, the significance of such a comparison is approaching to zero. Furthermore, in light of Fig. 12, there is absolutely no sense to discuss the agreement or disagreement of the profile shapes, since even the shapes of the profiles retrieved from different OSIRIS measurements have significantly different shapes.

The results presented in [Rivière et al., 2003] can not be directly used for the comparison because they are shown as OClO volume mixing ratios at pressure levels. In order to be able to discuss these profiles they have to be plotted in concentrations as function of the altitude and the source of the pressure and temperature profiles used for the conversion has to be referenced.

Finally, only the shape of the OClO profile presented in [Renard et al., 1997] is similar to that of the OSIRIS profile. Concerning the peak values, one should actually compare 7.3 $\pm$ 2 molec/cm^{-3} as retrieved from OSIRIS measurements to 8.7 $\pm$ 2 molec/cm^{-3} reported in [Renard et al., 1997] which do not actually differ within the error bars. Taking into account that according to [Solomon et al., 1990] the OClO column abundances in the late afternoon twilight are almost twice as large as the morning twilight values it is absolutely unclear how the evening values measured by OSIRIS have to be related to the nighttime values. Moreover, the "reference" nighttime values were obtained 7 years ago in the other hemisphere.

Concluding the discussion above, the comparison with the ground based measurements summarized in Table 8 has to be either completely reconsidered or removed from the paper.

ACPD

5, S1037–S1048, 2005

Interactive Comment

29. Section 4, page 3015, line 20: "On the other hand, nighttime OClO slant column abundances were found higher than diurnal measurements since photolysis is the main destruction mechanism for this species (e.g. Wahner et al., 1989)."

The sentence along with the reference is inappropriate since the measurements performed by OSIRIS are twilight measurements and, thus, according to [Solomon et al., 1990] they can result in much larger OClO abundances compared to diurnal measurements.

30. Section 4, page 3015, line 25: "Using the potential vorticity isoline of -48×10^{-6} K m^2 kg^{-1} s^{-1} at the 475 K isentropic level to define the edge of the polar vortex"

If you exert yourself so much for describing the vortex edge definition it would be useful to plot it, for example, in Fig. 12.

31. Section 4, Fig. 11: It is not quite precise to designate a comparison of a measurement at 81.7°S with a measurement at 45.1°S as a comparison of measurements inside and outside the vortex.

32. Section 4, page 3015: "Temperatures below the threshold of the PSC formation (i.e., typically $<$ 196 K) are observed between 14 and 23km of altitude where the largest OClO concentrations are detected."

This statement is contrary to the rapid decrease of OClO amount above 18 km. According to this consideration one can expect an OClO profile shape as predicted by REPROBUS (see Fig. 10), i.e., the OClO amount should be smoothly decreasing with the altitude form 18 to 23 km.

33. Section 4, page 3016: The motivation to present the profiles of ozone and NO_2 in Fig. 11 is too weak. It is obvious to expect reduced O_3 and NO_2 values inside the polar vortex. Thus, it is unclear if authors are trying to check the consistency of [Haley et al., 2004] retrievals or to prove if the measurement was really performed inside the vortex. This issue has to be clarified.

34. Section 5, Fig. 12: The plots referencing is wrong: top, middle and bottom panels.

35. Section 5, page 3016, line 26: "The evening twilight concentrations are larger than the morning abundances, in accordance with the results found by several authors (e.g., Sanders et al., 1989; Perner et al., 1991)."

Comparing the Scan B in the Fig. 12 with the profile shown in Fig. 10 which are both evening profiles obtained at nearly the same solar zenith angle one see that the peak values differ by factor of about 2 and the peak values of the profile shown in Fig. 10 are similar to that of Scan A profile in Fig. 12. Thus one can conclude that the difference in the OClO concentrations is more probably related to the geolocation rather than to the local time.

Considering an "accordance with the results found by several authors" one find in [Sanders et al., 1989] that the morning and evening vertical column abundances of OClO presented there refer to 90° solar zenith angle and "... were derived from measurements of the change in slant column abundance by assuming that the vertical column of OClO is constant with increasing zenith angles from about 84° to 90°." This does not have a lot in common with the OSIRIS measurements. Considering the slant column densities of OClO for morning and evening measurements presented in [Perner et al., 1991] no clear relation between morning and evening values can be identified. The only advice concerning the differences in the morning and evening vertical column abundance of OClO at solar zenith angles about 92° can be found in [Solomon et al., 1990]. According to this paper one can really expect the evening vertical abundances of OClO to be twice as large as the morning values. However, a vertical integration of the Scan A and Scan B profiles shown in Fig 12 results in nearly the same vertical column abundances for both profiles.

A relation between morning and evening concentrations could be much more easily investigated comparing the Scan A and Scan B profiles shown in Fig 12 with appropriate profiles modeled by REPROBUS.

36. Section 5, page 3017, line 16: “An area with large ClO concentrations is observed at altitudes 15 below 20 km (panel d), adhering well with the OClO abundances.”

In light of this statement, authors have to explain why the maxima in ClO concentrations at about - 70° latitude in the left side of the plot and about - 63° latitude in the right side of the plot are not associated with any detectable OClO concentrations. The same question arises concerning the increased ClO concentrations at about 20 km altitude.

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