Response to anonymous referee #3

Lorena Moreira

June 30, 2017

We are very grateful to Referee #3 for the useful and valuable comments which provided insights that helped significantly to improve the manuscript. All proposed objections and suggestions have been taken into account and discussed. Below we try to answer every comment. The changes in the manuscript are shown in blue and the text simply removed is crossed out in red.

More specific comments

- 1. Comments from the referee: Page 1, line 4: "for the retrieval of" is odd wording: "A new version of the ozone profile retrievals..."
 - Author's response:

No comments.

- Author's changes in the manuscript: Page 1, line 3–4: A new version of the ozone profile retrievals has been ...
- 2. Comments from the referee: Page 1, line 8: Shouldn't it be "GROMOS and Aura MLS profiles agree within 3% on average for ...", or "Average GROMOS and ..." or "On average, GROMOS and ..."?
 - Author's response:

No comments.

- Author's changes in the manuscript: Page 1, line 8: On average, GROMOS
- 3. Comments from the referee: Page 1, lines 12/13: The sentence that spans these lines is poorly worded. "This behavior is related to ..." is probably better. Also "On the other hand" is an inappropriate way in which to begin the sentence that follows.
 - Author's response:

We agree on the referee's comment. The text has been modified according to it.

Author's changes in the manuscript: Page 1, lines 12/13: This behavior is related to ...

Page 1, lines 13/15: On the other hand, the amplitude of the diurnal variation, night-to-day ratio (NDR), is not as strong as the observed one at higher latitudes, nevertheless we observe the winter anomaly of the night-to-day ratio.

4. Comments from the referee: Page 1, line 19: "its" \rightarrow "their"

Author's response:

Thanks for spotting. We have corrected this.

- Author's changes in the manuscript: Page 1, line 19: information about their distribution ...
- 5. Comments from the referee: Page 1, line 22: The assertion that this family of measurements have been indispensable would benefit from some citations that back that point up.

Author's response:

No comments.

- Author's changes in the manuscript: Page 1, line 22: Measurements of ozone performed by this technique have been indispensable in monitoring changes in the ozone layer and improving the comprehension of the processes that control ozone abundances (e.g. Steinbrecht et al. 2009).
- 6. Comments from the referee: Page 2, line 2: This sentence would also benefit from citations also (e.g., to some of the foundation documents for NDACC, or to GCOS [or similar] reports).

Author's response: No comments.

- Author's changes in the manuscript: Page 2, line 2: Continuous long-term monitoring of ozone is essential for the detection of long-term trends of the stratospheric ozone layer (e.g. WMO, 2014).
- 7. Comments from the referee: Page 2, line 10: "Furthermore" is inappropriate here. It's generally used when introducing a third or greater point, not for a second point. I suggest "In addition, we have ..." or "We have also,..."

Author's response:

No comments.

Author's changes in the manuscript: Page 2, line 10: We have also performed ...

8. Comments from the referee: Page 2, line 11: Badly constructed sentence. As written it sounds like there are two diurnal variations, one unspecified one, and one in mesospheric ozone, the amplitude of which you investigated.

Author's response:

No comments.

- Author's changes in the manuscript: Page 2, line 11: We have also performed an analysis of the diurnal variation and its amplitude (night-to-day ratio) of middle mesospheric ozone, at 0.05 hPa (70 km).
- 9. Comments from the referee: Page 2, line 13/14. This explanation could be more complete, specifically, it would be good to give the timescale for the recombination. Presumably it's ~ hours not ~ minutes, but needs to be made clear.

Author's response:

We have changed the sentence.

- Author's changes in the manuscript: Page 2, line 13/14: Daytime production of atomic oxygen by photolysis of ozone (Reaction 7) and photolysis of molecular oxygen (Reaction 5) results in nighttime ozone production by recombination of atomic and molecular oxygen (Reaction 6).
- 10. Comments from the referee: Page 2, line 14: "Moreover" feels like the wrong word here. "In addition..." might be better.
 - Author's response: No comments.
 - Author's changes in the manuscript: Page 2, line 14: In addition, we observe
- 11. Comments from the referee: Page 2, line 18: "an effect occuring at" \rightarrow "a phenomenon that occurs at"
 - Author's response: No comments.
 - Author's changes in the manuscript: Page 2, line 18: ... the MMM is a phenomenon that occurs at ...
- 12. Comments from the referee: Page 2, line 22: comma needed between "and" and "since"

Author's response:

No comments.

- Author's changes in the manuscript: Page 2, line 22: ... 185 nm and, since photolysis ...
- 13. Comments from the referee: Page 2, lines 23/24: Badly worded sentence. Suggest: "The lack of odd-hydrogen needed for the catalytic depletion of odd-oxygen, in conjunction with an unchanged rate of odd oxygen production, leads to an increase in odd-oxygen".

Regarding the discussion in this section of the paper, the more conventional way to frame it is to list some relevant reactions and then talk about the processes that give rise to maxima and diurnal cycles etc. in terms of those reactions. So we'd have sentences along the lines of "Lack of sunlight inhibits generation of odd hydrogen via reaction X, leading to enhancement in odd oxygen abundances due to continued production by reaction Y", or something similar. The authors might want to consider taking that approach.

Author's response:

We agree on the referee's comment. The text has been modified according to it.

Author's changes in the manuscript: Page 2, lines 20/24: Marsh et al. (2001) interpreted the tertiary peak by considering that in the middle mesosphere during winter, with solar zenith angle close to 90°, the atmosphere becomes optically thick to UV radiation at wavelengths below 185 nm and, since photolysis of water vapour (Reaction 1) is the primary source of odd-hydrogen, reduced UV radiation results in less odd-hydrogen. The lack of odd-hydrogen needed for the catalytic depletion of odd-oxygen (Reactions 2, 3 and 4), in conjunction with an unchanged rate of odd oxygen production (Reaction 5), leads to an increase in odd-oxygen. This results in higher ozone concentration because atomic oxygen recombination (Reaction 6) remains as a significant source of ozone in the mesosphere. Additionally, Hartogh et al. (2004) extended the interpretation by considering the very slow decrease of the ozone dissociation (Reaction 7) rate with increasing solar zenith angle.

$$H_2O + h\nu(\lambda < 185nm) \longrightarrow OH + O \tag{1}$$

$$O + OH \longrightarrow O_2 + H$$
 (2)

$$H + O_2 + M \longrightarrow HO_2 + M$$
(3)

$$O + HO_2 \longrightarrow O_2 + OH$$
 (4)

$$O_2 + h\nu(\lambda < 242nm) \longrightarrow O + O \tag{5}$$

$$O + O_2 + M \longrightarrow O_3 + M \tag{6}$$

$$O_3 + h\nu \longrightarrow O_2 + O \tag{7}$$

14. Comments from the referee: Page 3, Section 2.1. This section would benefit from having a few more details concerning the instrument. In particular, no information is given on the bandwidth of the observed spectrum, the spectral resolution, or the receiver noise temperature etc. These are all key parameters needed to get a sense of the measurement system. A plot showing a sample spectrum and associated error bars would be most welcome. For example, there's little point talking about adding 0.5K to the noise here or there without giving the reader a sense of how big the $T_{rec}/sqrt(B tau)$ number is. At what altitude does Doppler broadening start to dominate over pressure broadening for this line? Also, presumably the retrievals need to assume a temperature (and height?) profile. Some information on where that is taken from, and the sensitivity of the result to it would be useful to give.

Author's response:

The referee is right to ask about more details concerning the instrument, yet for these details we refer to Moreira et al. (2015).

This 0.5 K added to the noise is due to spectroscopic errors and the water vapour continuum.

The Doppler broadening starts to dominate above 75 km, in case of ozone at 142 GHz.

We agree on the referee's comment about more information on the temperature and pressure profiles needed for the retrieval. The text has been modified according to it.

Author's changes in the manuscript: Page 3, line 18: In addition, a constant error of 0.5 K is considered as a systematic bias of the spectra, due to spectroscopic errors and the water vapour continuum.

Page 3, line 9: The a priori profile required for the retrieval is taken from a monthly varying climatology from ECMWF reanalysis until available (70 km) and extended above by an Aura MLS climatology (2004 to 2011). The line shape used in the retrieval is the representation of the Voigt line profile from Kuntz (1997). Spectroscopic parameters to calculate the ozone absorption coefficients were taken from the JPL catalogue (Pickett et al., 1998) and the HITRAN spectroscopic database (Rothman et al., 1998) The atmospheric temperature and pressure

profiles are taken from the 6 hourly of the European Centre for Medium-Range Weather Forecast (ECMWF) operational analysis data and are extended above 80 km by monthly mean temperatures of the CIRA-86 Atmosphere Model (Fleming et al., 1990).

15. Comments from the referee: Page 3, line 8: Is the ozone a priori really taken from the ECMWF analysis? How useful is that up to 70km, what is it based on. A reference would be good.

Author's response:

Yes, it is. The a priori ozone profile does not play a role since the measurement response, area of the averaging kernels, is equal to unity for the altitude range from 18 to 70 km.

Author's changes in the manuscript: No changes.

16. Comments from the referee: Page 3, line 13: You tell us that v150 has a constant a priori, but don't say how it behaved in 2021, it would be useful to know.

Author's response:

In version 2021, as diagonal elements of the a priori covariance matrix we assume a relative error around 35% at 100 hPa. The error decreases in the lower stratosphere up to 28%. Then it increases linearly from 35% in the upper stratosphere to 70% in the lower mesosphere. The off-diagonal elements exponentially decrease with a correlation length of 3 km.

We have performed a comparison between version 2021 and version 150 of the retrieval of GROMOS.

Author's changes in the manuscript:

Page 3, line 12: Recently, we have developed a new retrieval version (version 150) with the aim to optimise the averaging kernels. The differences with the former version (version 2021) are in the a priori covariance matrix, in the measurement error and in the integration time of the retrieval.

In version 2021 the diagonal elements of the a priori covariance matrix are variable relative errors ranging from 35% at 100 hPa to 28% in the lower stratosphere and increasing with altitude from 35% in the upper stratosphere up to 70% in the mesosphere. Meanwhile, in version 150 the a priori covariance matrix has a constant value for the diagonal elements of 2 ppm. For both retrieval versions the off-diagonal elements of the a priori covariance matrix exponentially decrease with a correlation length of 3 km.

Regarding the measurement noise, in version 2021 it is a constant error of 0.8 K whereas in version 150 we used a variable error depending on the tropospheric transmission:

$$\Delta T_b' = 0.5 + \frac{\Delta T_b}{e^{-\tau}} \tag{8}$$

the error of the measured brightness temperature, ΔT_b , is given by the radiometer equation:

$$\Delta T_b = \frac{T_b + T_{rec}}{\sqrt{\Delta f \cdot t_{int}}} \tag{9}$$

The radiometer equation gives the resolution of the radiation measured, which is determined by the bandwidth of the individual spectrometer channels (Δf) , by

the integration time (t_{int}) and by the total power measured by the spectrometer. A constant error of 0.5 K is considered as a systematic bias of the spectra, due to spectroscopic errors and the water vapour continuum. The error of the brightness temperature (ΔT_b) is of the order of a few Kelvins in the line centre and 0.5 K in the line wings of the spectrum. Therefore the measurement noise $(\Delta T'_b)$ depends on the bandwidth of the spectrum and on the tropospheric transmittance. This is a more realistic approach for the retrieval than considering a constant measurement noise, resulting in an improvement in the retrieved ozone VMR in the lower stratosphere. The sampling time for version 150 is 1 hour and in case of version 2021 is 30 minutes. Longer integration time improves the retrieved ozone VMR at upper altitudes.



Figure 1: Mean ozone profiles retrieved by version 2021 (red line in the left panel) and by version 150 (blue line in the left panel) measured by GROMOS during the period from July 2009 to November 2016. The blue area (v150) and the red area (v2021) are the standard deviations of the ozone VMR. The mean relative difference profile (blue line) and the standard deviation of the differences (blue area) are represented in the middle panel, using the new version as reference. The green line delimits the $\pm 10\%$ area. In the right panel is shown the VMR difference profile along with its standard deviation

Page 4, line 1: In version 2021, the vertical resolution lies generally within 10–15 km in the stratosphere and increases with altitude to 20–25 km in the lower mesosphere. Between 20 to 52 km (50 to 0.5 hPa) the measurement response is higher than 0.8. For more details on version 2021 we refer to Moreira et al. (2015). Comparing the measurement response and the vertical resolution obtained by version 2021 and by version 150 we can conclude an improvement in the results retrieved by version 150. We assume that the changes performed in the a priori covariance matrix, in the measurement noise and in the integration time result in the improvement of the retrieval product, mainly observed in the lowermost and in the uppermost limit of the retrieved ozone VMR profile.

17. Comments from the referee: Page 3, line 13: "optimizing" in what sense, what

were you trying to optimize? The vertical range, resolution, what? [Or should you change the "and" on the same line to "by"?]

Author's response:

No comments.

- Author's changes in the manuscript: Page 3, line 13: ..., thus optimizing the averaging kernels by improving ...
- 18. Comments from the referee: Page 3, line 15: This discussion is a little confusing. Earlier parts of the paper give the impression that this study of the diurnal cycle was, at least partly, enabled by the new GROMOS data version. However, here you talk about the new version being focused on improvements in the lower stratosphere. If there were improvements in the mesosphere, it would be best to be more specific about what they are and which of the changes (presumably among those discussed above) brought those improvements about.

Author's response:

No comments.

- Author's changes in the manuscript: Page 3, line 15: ... the measurement response in the lower stratosphere and in the mesosphere.
- 19. Comments from the referee: Page 3, lines 17/18: You need to define all of the terms in these equations, and give us the numbers for T_{rec} , B and tau.

Author's response:

We have changed the sentence.

- Author's changes in the manuscript: Page 3, lines 17/18: The error of the measured brightness temperature, ΔT_b , is due to noise fluctuations in the spectrum and is of the order of a few Kelvins in the line center and 0.5 K in the line wings of the spectrum.
- 20. Comments from the referee: Page 3, line 23: "The AVKs are multiplied by 4 in figure 1 in order to ..."

Author's response:

Thanks for spotting. We have corrected this. Former Figure 1 is now Figure 2.

- Author's changes in the manuscript: Page 3, line 23: The AVKs are multiplied by 4 in Figure 2 in order ...
- 21. Comments from the referee: Page 3, line 24: AVK \rightarrow AVKs

Author's response:

No comments.

Author's changes in the manuscript: Page 3, line 24: AVKs ...

22. Comments from the referee: Page 4, line 5 (your numbers): "our location" \rightarrow "Bern" or "the GROMOS measurement location" or similar.

Author's response:

No comments.

Author's changes in the manuscript: Page 4, line 5: The satellite overpasses the GROMOS measurement location (at northern midlatitudes) twice a day

23. Comments from the referee: Page 4, Line 13: Suggest you make this a "displayed" equation rather than an "inline" one. Also, conventionally vectors are in lower case. If using LaTeX suggest _{GROMOS} (amsmath.sty) rather than _{GROMOS}, it give more suitable letter spacing (similarly for MLS).

Author's response:

No comments.

Author's changes in the manuscript: Page 4, Line 13: The smoothed profile of MLS adjusted to the vertical resolution of GROMOS is expressed as:

 $\mathbf{x}_{\text{MLS,low}} = \mathbf{x}_{\text{a,GROMOS}} + \mathbf{AVK}_{\text{GROMOS}} \cdot (\mathbf{x}_{\text{MLS,high}} - \mathbf{x}_{\text{a,GROMOS}})$ (10)

being AVK_{GROMOS} is the averaging kernel matrix of GROMOS, $\mathbf{x}_{MLS,high}$ is the measured Aura/MLS profile and $\mathbf{x}_{a,GROMOS}$ is the a priori profile ...

24. Comments from the referee: Page 4, Line 15: Surely Tsou is not the first such reference. Cite others, or at least put "e.g.," in front.

Author's response:

No comments.

Author's changes in the manuscript: Page 4, Line 15: by e.g. Tsou et al. (1995).

25. Comments from the referee: Page 4, line 19: More major point here. 8°/800 km is a very large coincidence window, particularly given the ~165km along track spacing for MLS measurements. While you might need this on some days, when GROMOS falls in the gaps between the MLS orbits, on other days you'll get ~5 coincident observations. However, you do not tell us what you do in such circumstances. Do you compare your one GROMOS profile to all five? Do you pick the closest one? Do you average the five profiles together to give one comparison? What are the impacts of your choice on the subsequent analyses? More detail is needed here if readers are to be able to correctly interpret the results that follow.

Author's response:

We have performed major changes in the comparison method. The criterion for spatial coincidence is now that horizontal distances between the sounding volumes of the satellite and the ground station have to be smaller than 1° in latitude and 8° in longitude. Then, I have one profile of MLS to compare to one profile of GROMOS every time the temporal and spatial criteria is fulfilled. We define as nighttime (daytime) value the average between the values recorded within 2 hours around midnight (noon).

- Author's changes in the manuscript: Page 4, line 17: The selected criterion for spatial coincidence is that horizontal distances between the sounding volumes of the satellite and the ground station have to be smaller than 1° in latitude and 8° in longitude.
- 26. Comments from the referee: Page 4, line 30: I'm a little bit wary of using the term absolute difference, more particularly in the caption for Figure 2, where you use the term "mean absolute difference". It could be taken to mean the mean of the unsigned difference, |a-b|. Perhaps simply say "mixing ratio difference"?

Author's response:

We agree on the referee's comment.

- Author's changes in the manuscript: We have changed mean absolute difference for mean VMR difference everywhere.
- 27. Comments from the referee: Page 5, lines 2 and 3 (counting from -2): At face value, the 30-day smoothing and 4-day filtering appear to be contradictory. If the 30 data points are for 30 days worth of observations, then surely such a smoothing is going to filter far more aggressively than 4 days? Are there more than 30 points per day? Is this related to the issue of having more multiple MLS matches to a single GROMOS measurement? If so, this needs to be made much clearer. Plus, the impact of this smoothing is going to vary quite significantly depending on how many points there are on a given day. Why not simply smooth on a daily rather than a point-by-point basis (average of all differences within an n-day window)? Again, all this needs to be much more clearly described.

Author's response:

As we have changed the spatial criteria of coincidence the number of coincident profiles has changed as well. Therefore, now we have performed moving average over 7 points which corresponds to around 1 week. Performing a daily smoothing in the time series will produce noisy and unclear Figures and hence difficulties to interpret them.

Author's changes in the manuscript: Page 5, lines 2 and 3: Short temporal fluctuations (periods < 4 days) are suppressed by a moving average over 30 data points of both time series. All time series have been smoothed by a moving average over 7 points (\sim 1week).



Figure 4: Time series of averaged daytime and nighttime O_3 VMR measurements of GROMOS (blue line) and MLS (red line) for the period from July 2009 to November 2016 at different pressure levels. An averaging kernel smoothing has been applied to the series of the MLS measurements coincident in time and space with the GROMOS measurements. Both time series are smoothed over 7 points or 1 week in time by a moving average

28. Comments from the referee: Page 5, line 8: "almost perfect" is very much in the eye of the beholder, and in my eye your scatter plots are far from it. To me "almost perfect" is at the > 0.999 level of correlation, where the points are all but indistinguishable from the 1:1 line, with perhaps just one or two strays. I suggest you use more measured language.

Author's response:

No comment.

Author's changes in the manuscript: Page 5, line 8: An almost perfect agreement

29. Comments from the referee: Page 5, line 9: Odd way to phrase it, simply say that the black line is close to the green one to one line.

Author's response:

We agree with the referee.

- Author's changes in the manuscript: Page 5, line 8–9: The black lines, linear regression lines of the observations, are close to the green one to one lines, $O_3(MLS)=O_3(GROMOS)$.
- 30. Comments from the referee: Page 5, line 21: "variation is also expected"

Author's response:

Thanks for spotting. We have corrected this.

- Author's changes in the manuscript: Page 5, line 21: ... therefore an annual variation is also expected
- 31. Comments from the referee: Page 6, lines -2 to 2: As discussed above, more discussion is needed here. Some more investigation is needed as to why the amplitudes of the cycles are so different. You don't even tell us if we should be surprised by this level of disagreement. Note that the MLS averaging kernels imply not insignificant vertical smoothing at these altitudes for this instrument too. When taken in conjunction with the possible latitudinal gradient, are there plausible reasons to explain the differences based on sampling etc. alone, or is the only feasible explanation some instrumental/calibration difference? If nothing else, raise these questions and identify a route to answering them. Could the diurnal cycle in temperature (and thus the pressure/height relationship) play any role in this (from a measurement characteristics point of view rather than an atmospheric science one)? This manuscript would greatly benefit from an analysis, or at least an identification, of all the potential factors involved.

Author's response:

According to Sonnemann et al. (2007), the MMM is an effect occurring at high latitudes close to the polar night terminator around 72 km altitude during nighttime in the winter half of the year and extends into middle latitudes with decreasing amplitude. The observed sharp decrease of the amplitude of the MMM of ozone is due to the strong latitudinal gradient between high and middle latitudes. In fact, it is surprising that we can observe the effect of MMM at our latitude. Therefore, the difference in latitude between Lindau and Bern may have such impact in the amplitudes of the annual variability of mesospheric ozone due to the MMM. However it could also be due to some other effects like for example, differences in the retrieval algorithms between Bern and Lindau, different instruments used to perform the measurements, different calculation methods...

- Author's changes in the manuscript: Page 6, line 4: Nevertheless, our results are the expected since this maximum of mesospheric ozone during nighttime in winter is related to the middle mesospheric maximum of ozone (MMM) and according to Sonnemann et al. (2007) its effect extends into midlatitudes with decreasing amplitude.
- 32. Comments from the referee: Page 6, lines 13-15: This discussion is unclear, at least to me. If the orange points are smoothed by 10 points, is that 10 days? How does this number related to the ~7 years between 2009 and 2016. I don't get how the 10-point and 30-point smoothings are related.
 - Author's response:

We have repeated the comparison by changing the spatial criteria of coincidence and now the number of coincident profiles has changed. In the first panel of Figure 7 (former Figure 6) the moving average is over 30 points, roughly 1 month and in the second panel we used a moving average over 7 points which corresponds to around 1 week. The purpose of the smoothing is to help the interpretation of the results.

Author's changes in the manuscript: Page 5, line 30: All time series displayed in both panels of Figure 6 have been smoothed in time by a moving average over 15 data points (~ 1 week).

Page 6, lines 13-15: ...under assessment. Both time series were smoothed in time by a moving average over 30 points ($\sim 1 \text{ month}$). ... the second panel of Figure 7 show a moving average over 7 data points (1 week) with the aim to clarify the understanding of Figure 7. The Aura/MLS and the GROMOS series depicted in Figure 5 and Figure 6 have been smoothed in time by a moving average over 30 data points.

33. Comments from the referee: Figures: In general, all the figures use overly heavy line thicknesses. While it may be OK for the lines themselves (though rather on the heavy side), the line width used is far to heavy for the axes. Also the font should be slightly (~20-50%) larger, and perhaps not bold, for greater clarity. Figure 2: Suggest "mean absolute difference" → "mean mixing ratio difference". Also, how is 'its uncertainty" (last line) defined? Do you mean standard deviation?

Author's response:

We have calculated the mean relative difference profile and the VMR difference profile separating daytime and nighttime values, accordingly Figure 3 (former Figure 2) has changed.

Author's changes in the manuscript: Figure 3



Figure 6: The first panel shows the diurnal variation of O_3 VMR measured at noon (GROMOS in red, MLS convolved in orange and MLS original in magenta) and at midnight (GROMOS in blue, MLS convolved in cyan and MLS original in black) at 0.05 hPa (70 km) and the second panel shows its evolution throughout the year averaged for the time interval under assessment (July 2009–November 2016). All time series are smoothed in time by a moving average over 15 points (1 week)



Figure 7: The first panel displays the night-to-day ratio (NDR) of GROMOS (blue line) and MLS (red line) at 0.05 hPa (70 km) for the time period from July 2009 to November 2016 and the second panel shows its evolution throughout the year averaged for this time period. The time series presented in the top panel are smoothed in time by a moving average over 30 data points (1 month) and the orange line (MLS) and the cyan line (GROMOS) shown in the second panel are averaged over 7 data points (1 week)



Figure 3: Mean ozone profiles recorded by GROMOS (blue line), MLS convolved (red line) and MLS original (green line) for the time interval between July 2009 and November 2016 are shown in the left panels of both daytime and nighttime Figures. The blue area (GROMOS) and the red area (MLS) are the standard deviations of the coincident measurements. The middle panels show the mean relative difference profile between data of both instruments, GROMOS as reference. The blue areas in the middle panels represent the standard deviation of the differences. The green lines in the middle panel delimit the \pm 10% area. The mean VMR difference profile and its standard deviation (blue area) are displayed in the right panels of both daytime and nighttime, Figure 3a and Figure 3b, respectively