Reply to comments of anonymous referee #1 on the manuscript "An improved glyoxal retrieval from OMI measurements" by L. M. A. Alvarado et al.

We would like to thank the anonymous referee #1 for his/her valuable comments.

Major comments

- Some important aspects are currently missing in the description of the algorithm. What is the reference spectrum for the DOAS analyses? The OMI daily measured irradiance spectrum, the consolidated OMI sun spectrum or a radiance spectrum measured in a remote area? Does a wavelength calibration procedure need to be applied to the OMI spectra? Is an intensity offset fitted? Also OMI suffers from the so-called row anomaly after 2007. How do you deal with this?

In our retrieval, a mean reference spectrum has been used (the consolidated OMI sun spectrum). Moreover, a two-step wavelength calibration has been applied which first aligns the irradiance spectrum to a high resolution Fraunhofer spectrum (Chance and Kurcz, 2010) and then the radiance spectrum to the irradiance. An intensity offset is fitted as well. Additionally, the quality flags provided by NASA are used to reduce the problem with the row anomaly.

Please see sect. 2.2

- Section 2.3 For the water vapour cross-section, a reference to Rothman et al., 2005 is given. The HITRAN database, including the water vapour line shape parameters, has been updated several times since the version of 2005. Interferences with the water vapour may have a significant impact on the retrieved glyoxal slant columns. Is there a good reason to keep using HITRAN 2005 for the water vapour or is it only the reference that needs to be updated?

We agree with the reviewer that water vapour is an important parameter in glyoxal retrievals, at least from the ground. Therefore, we have added a new section (sect. 2.8) in the revised manuscript with sensitivity tests using different water vapor cross-sections. However, no significant improvements have been found using a different HITRAN version than the 2005 data used originally. For example, if we estimated the relative difference in the chisquare using HITRAN 2005 and HITRAN 2012, the largest differences are around 1.0 % (see Fig. 1), which does not signify significant improvement in the retrieval (see sect. 2.8).

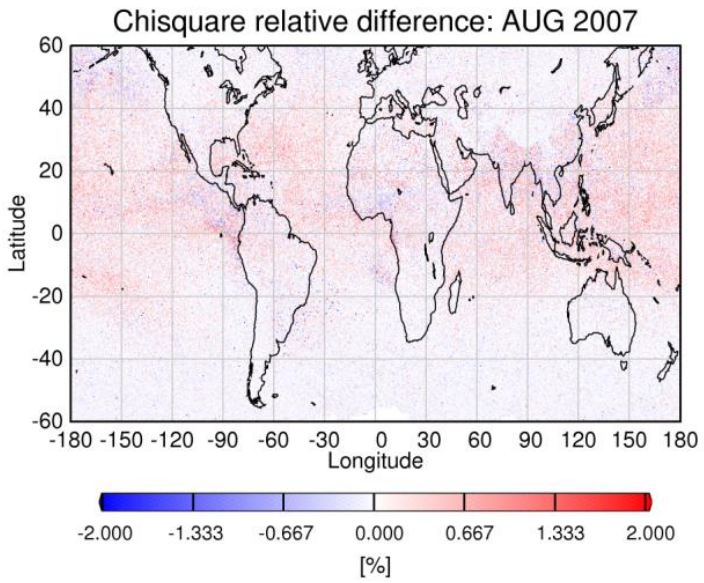


Fig. 1: Monthly chisquare relative difference between glyoxal retrievals using water vapor cross-section from database HITRAN 2005 and HITRAN 2012 for August 2007.

- Section 2.4:

  - It can be inferred from the different figures that these tests are based on a polynomial of degree 3 without any specific correction for the liquid water interferences. This should be explicitly mentioned in the text.

This has been specified in the revised manuscript as suggested.

  - In figure 1, the choice of the reference value to compute the relative differences is strange. Usually, the "truth" is the reference. Please compute the differences as (SC_fitted - SC_true)/SC_true. Please mention also this true value.

The relative differences have been recomputed and changed in the revised manuscript. However, no changes are observed in the result. Also, the "true value" has been added in the text (2.69×10^{15} molec.cm^{-2}).

  - The deviations observed from the closed-loop tests are rather small. This is expected as the same cross-sections are probably used for both creating the synthetic spectra and retrieving the slant column. So errors due to spectral interferences and use of imperfect cross-sections can't be estimated using this technique. On the other hand, the authors should discuss the origin of the deviations, even if they are small, and their dependence on the fitting interval. What are the differences between the forward model used to create the synthetic spectrum and the DOAS model. How is the Ring effect simulated?

We agree that errors due to spectral interferences cannot be estimated using this technique. We assumed that the cross-sections are perfect, which is not true, but we do not know in which way they are imperfect and thus this technique is only used for obtain information on the optimal wavelength retrieval.

Discussion on the origin of deviations has been added in the text.

The forward model uses full multiple scattering and the temperature dependence of cross-sections is included, while the DOAS model is based in the Beer-Lambert law where the effect of scattering is simulated using a polynomial function.

No ring effect is simulated in the forward model.

- The fact to have deviations in the closed-loop tests so small compared to those observed with real data raises some questions about their added value to the discussion. Is it possible to make a link between these two aspects?

We see the main added value for the choice of fitting window and the illustration of polynomial effects on perfect data. We agree that in view of the much larger variations in real data the synthetic data do not appear to include the most important interfereing effects. We think that this is also an important result. In addition we assumed that not having such a study in our paper would have prompted requests from the reviewers to include it…

- Why different dates had to be used for the different regions?

Different dates have been used as, hot-spots with large glyoxal amounts have been chose and due to many factors, these high values cannot be found for the same day. However, the pattern is quite similar for different days even if the amount of glyoxal is different.

- Section 2.5:

- See comments from previous section.

The revised manuscript has been modified accordingly.

- In figure 2, the deviation patterns significantly differ from a region to another. Is the impact of the polynomial degree the same for all regions? It might be useful to show at least one other region, which could possibly replace the tests based on the synthetic spectra.

In the revised manuscript we have added plots for another region, showing that the impact in the polynomial degree is quite similar for others regions. Moreover, we still keep the tests bases on the synthetic spectra as they help to explain in the clearest way why we should use the polynomial 3.

- Section 2.6:

  - If I understand correctly, a liquid water correction is only applied over oceanic regions. I think there is a risk of discontinuity between the retrieved glyoxal fields over oceans and lands. In theory, the liquid water signal should obviously be negligible over lands. In practice, spectral interferences with other species might lead to a bias in the retrieved liquid water SC. If there is such a bias, It would be better to have the liquid water cross-section also included for the treatment of pixels over lands to ensure a spatial homogeneity of the product. Did you check that the retrieved liquid water SC is small over lands (and consequently has no impact on the glyoxal)?

We agree with the reviewer that this is a problem that needs to be considered. In fact, the liquid water SC over land is small (Liquid Water SC, Fig. 2, left), but still has some impact on the glyoxal (Absolute difference, Fig. 2, right). These differences are small, around three times smaller than the detection limit, but systematic. They correspond mainly to those regions where the liquid water SCs are negative (Liquid water SC, negative points are shown in black, Fig. 2, left). Moreover, some differences are found over high mountains (Himalaya) and also over deserts most likely due to interferences with soil which has similar spectral feature as the liquid water and unphysical results can be obtained (Richter et al., 2011). The overall good agreement as well as the larger differences over some areas is shown in the longitudinal variations across the African continent (Fig. 3).

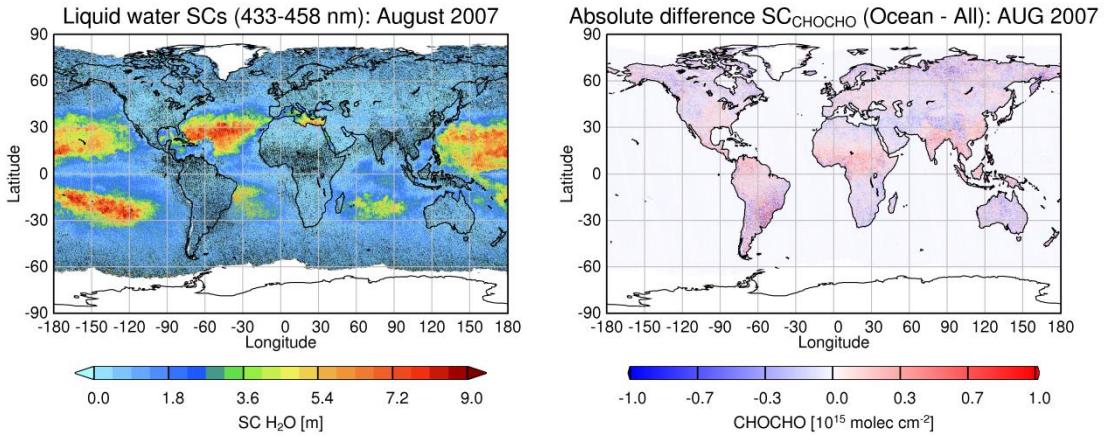


Fig. 2: Monthly mean of liquid water SCs retrieved in the wavelength range of 433-458 nm (left) and the absolute difference of glyoxal SCs between the retrieval that include the liquid water cross-section only over ocean and the one that include over all (right) for August 2007.

Considering the differences between the two retrievals, the question is which of the two provides the better glyoxal results. Over the oceans, using the liquid water cross-section is certainly to be preferred, as otherwise large artefacts are introduced over clean water regions.

Over land, any liquid water signal found, in particular with a negative slant column, has to be explained by spectral interference. Changes in glyoxal column related to these signals could be explained by either spectral interference between glyoxal and liquid water differential cross-section, or by the chance removal of other spectral signatures by the liquid water cross-section. While no firm conclusion can be drawn, we consider it the more conservative approach not to include the liquid water cross-section over regions where we know that this signal is not present, even if that has the potential to introduce a bias relative to the glyoxal retrievals over the oceans.

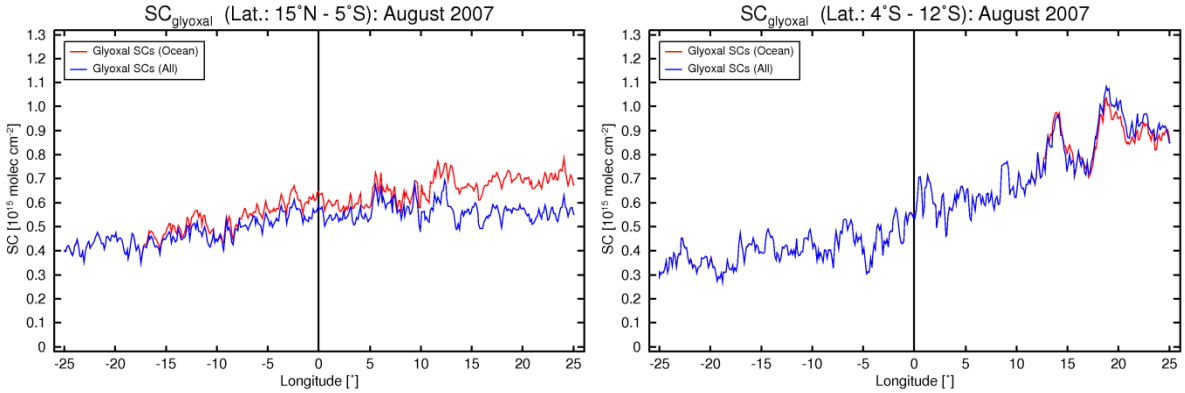


Fig. 3: Comparison of latitudinal variation of CHOCHO SCs for retrievals with include the liquid water cross-section only over ocean with the retrieval that include it over all (ocean and land) for African continent in August 2007.

- Some of the authors are also co-authors of the paper recently published in AMTD by Peters et al.. Did you try to apply the method proposed there to better account for all liquid water effects in glyoxal satellite retrievals?

Yes, we have tried to include the empirical cross-section of Peters et al. for the glyoxal retrieval. Unfortunately, no clear improvement is observed in the fitting window used, which is small in comparison of the wavelength range used for the test in the method proposed by Peters et al. Therefore, the Peters et al. cross-section was not included in our retrieval.

- Section 2.7:

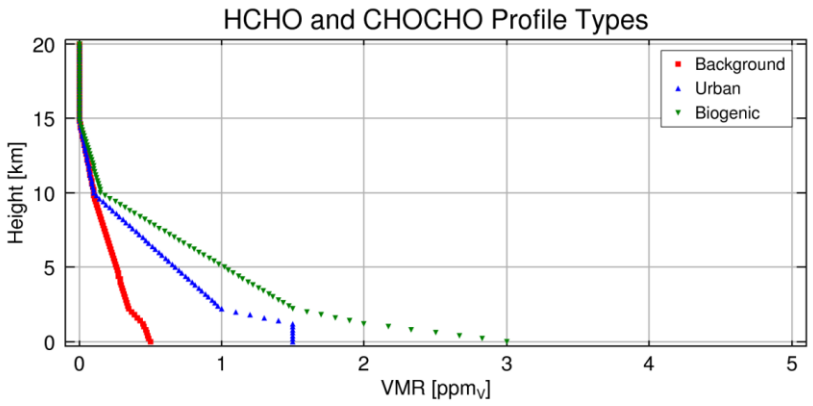
  - In figure 5: In order to better see the impact of including a second NO2 cross-section on the retrieved glyoxal columns, I would suggest to replace the second series of CHOCHO maps (third row) by maps of the CHOCHO absolute differences (2 NO2 cross-sections - 1 NO2 cross-section).

The plot has been replaced as suggested.

- Section 2.8 (Now sect. 2.10):

  - The authors refer to the Wittrock et al. paper for the typical glyoxal profiles used in the AMF computation. I unsuccessfully tried to find the information in this paper and in the references cited therein. For the sake of transparency, could you add a figure illustrating these typical profiles?

In the manuscript is cited "Wittrock, F.: The retrieval of the oxygenated volatile organic compounds by remote sensing techniques, Ph.D thesis, University of Bremen, 2006" (http://www.iup.uni-bremen.de/doas/paper/diss_wittrock_06.pdf). You can find these profiles on page number 96.



Profile types utilised to calculate the satellite AMF for formaldehyde and glyoxal. From Wittrock, 2006, p96

- Section 2.9 (Now sect. 2.11):

  - This section is quite general and could be made shorter by adding a few references. The authors suggest that the systematic errors are constant overtime. This is probably erroneous as a significant fraction of these systematic errors is caused by spectral interferences with other species, of which the concentration may depend on the season. As mentioned by the authors, the normalization procedure helps to reduce the impact on the glyoxal product of these interferences. Nevertheless, the spatial variability of these systematic errors remains. This should be clarified in the text and an estimate of the systematic errors should be given. Finally, is there a basis for the value of 2x1014 molec/cm2 used for the glyoxal background or is it somewhat arbitrary?

We agree with the reviewer and the section has been rewritten accordingly. Additionally, an estimation of systematic errors has been added.

Yes, the glyoxal background used is somehow arbitrary, because we do not know the real glyoxal level over the Pacific. However, this value is in agreement with the values found by Sinreich et al., 2010 over the remote tropical Pacific Ocean and also with the offset applied by Lerot et al., (2010).

- Section 3:

  - For these comparisons, the SCIAMACHY and GOME-2 data appear having been reprocessed using a second NO2 cross-section. Why did the authors not apply any correction for liquid water interferences for these two sensors? This inconsistency may lead to significant inter-sensor biases because of the normalization procedure. Indeed, the oceanic glyoxal fields will be strongly different for all three sensors, which means that the reference values removed from all measurements of the day (including lands) as part of the normalization will differ significantly, but do not reflect necessarily instrumental specificities. I wonder if the important SCIAMACHY bias could come from this.

We agree with the reviewer that liquid water correction is needed for the glyoxal retrieval from SCIAMACHY and GOME-2 measurements to be consistent. However, the liquid water correction does not work similarly for the three sensors and more sensitivity test are needed to come to the optimal correction. Despite that, the SCs retrieved from the SCIAMACHY sensor without the normalization were already higher than those of GOME-2 and OMI. In fact, the normalization can introduce bias but these are small and do not have significant impact in the final product.

  - A destriping correction is mentioned without any details. Please explain a bit more. What does it correct for? How does it work?

In the revised manuscript a new section about the destriping has been added (see Sect. 2.9).

  - To me, the three data sets do not compare so well. Differences could be expected between OMI on one hand and SCIAMACHY/GOME-2 on the other because of possible diurnal variation but large SCIAMACHY-GOME-2 differences such as those displayed in Fig. 8 are quite unexpected. This should be discussed a bit more. Is it because of the absence of correction for liquid water absorption in SCIAMACHY (see above)? On the other hand, the seasonal cycles of SCIA and GOME-2 roughly agree.

We agree with the reviewer that the consistency between the three glyoxal products is not as good as one would hope for. The liquid water correction - which has only been applied to OMI data - is one possible candidate for these differences, but applying it to GOME-2 and SCIAMACHY data did lead to problems in the retrievals (see above) and did not improve the

consistency between the data sets. We have to admit that up to now, we have been unable to improve on this point.

- Section 5:

  - How should negative correlation coefficients visible in figure 10 be interpreted?

The negative correlation coefficients correspond to regions dominated by biogenic emissions. In fact, these are regions with much vegetation and less impact of wild fires.

  - In figure 11, it would be interesting to show a similar CHOCHO map for another year in order to highlight the exceptional nature of the event.

A glyoxal map for 2009 has been added to figure 11 in the revised manuscript.

- Conclusions

  - "Significant differences were found over regions with large anthropogenic emissions. Moreover, a similar seasonal behaviour is observed among the three products." This is inconsistent with the text of section 3: "good agreement is found in the temporal behaviour among data sets over regions dominated by biogenic emissions and also with large anthropogenic activities, such as China (South and East)". In addition, the OMI seasonal cycle appears to differ from that of the two other products in several of the regions presented in figure 8 (it is generally less pronounced).

In the revised manuscript the section 3 has been rewritten and thus the conclusions have been changed accordingly.

Editorial comments

All editorial suggestions have been applied to the manuscript.

- Abstract - line 11 : "reduction of negative columns" is not a very clear formulation. Please rephrase.
- Page 5561 line 21: "Similarly to the biogenic and anthropogenic emissions" instead of "Similar to biogenic emissions". Anthropogenic emissions are certainly not better quantified.
- Page 5561 line 24: delete "various", "VOCs" instead of "VOC"
- Page 5562 - line 11: "spaceborne" instead of "space-born"
- Page 5562 - line 15: "have been used to derive CHOCHO distribution at the global scale by applying…" instead of "to retrieve global maps of CHOCHO distribution by applying…"

- Page 5563 - line 11: “a description of the method used to limit interferences with liquid…” instead of “a description of the interferences with liquid…”
- Page 5563 - line 14: Remove “glyoxal products” after SCIAMACHY and GOME-2.
- Page 5564 - line 10: “are removed by the fit of a low-order polynomial.” Instead of “are removed by a polynomial in wavelength”.
- Page 5564 - line 12: “by including corresponding absorption cross-sections in the DOAS fit” instead of “by taking into account the absorption cross-sections of all relevant trace gases.”
- Page 5564 - line 12: What is a “good DOAS fit”? Do you mean “to derive accurately SCs”?
- Page 5564 - line 19: rephrase as “460 nm, which includes different interference species, and use polynomial of order 2,3 or 4 for the removal of broad-band signatures (Wittrock et al., 2006; Vrekoussis et al., 2009).”
- Page 5564 - line 26: “a new retrieval algorithm for the OMI instrument…” instead of “a new retrieval for data of the OMI…”
- Page 5564 - line 27: “details” instead of “detailed”
- Page 5570 - line 6: Suggested sentence: “This result shows that the temperature dependence of the NO2 absorption cross-section needs to be taken into accountin case of large tropospheric NO2 columns to limit as much as possible (seasonal dependent) systematic errors on the glyoxal column caused by spectral interference.”
- Page 5570 - line 10: please rephrase. It is not only useful to compute vertical columns, but it is mandatory since the SCs are not directly applicable in any atmospheric application.
- Page 5571 - line 26 “of” instead of “ot”
- Figures 8 and 9: Specify explicitly from which sensor (OMI) are derived these maps.
- Section 4 and figure 9: Please avoid as much as possible to use the terms “summer”, “winter”, “autumn” and “spring” in the discussion since those terms are only valid locally.
- Page 5574 - line 1: remove “part of the”
- Page 5574 - line 7: replace “anthropogenic” by “highly populated”
- Page 5575 - line 8: “shown” instead of “show”
- Page 5575 - line 19: remove “days”
- Page 5576 - line 21: “reduction of negative glyoxal values” is not very clear. Please reformulate.
- Page 5576 - line 25: remove “at high NO2”

References

- Lerot, C., Stavrakou, T., De Smedt, I., Müller, J.-F., and Van Roozendael, M.: Glyoxal vertical columns from GOME-2 backscattered light measurements and comparisons with a global model, Atmos. Chem. Phys., 10, 12059-12072, doi:10.5194/acp-10-12059-2010, 2010.
- Richter, A., Begoin, M., Hilboll, A., and Burrows, J. P.: An improved NO_2 retrieval for the GOME-2 satellite instrument, Atmos. Meas. Tech., 4, 1147-1159, doi:10.5194/amt-4-1147-2011, 2011.
- Sinreich, R., Coburn, S., Dix, B., and Volkamer, R.: Ship-based detection of glyoxal over the remote tropical Pacific Ocean, Atmos. Chem. Phys., 10, 11359-11371, doi:10.5194/acp-10-11359-2010, 2010.