Reply to review #1 of our manuscript number amt-2021-158 'Glyoxal tropospheric column retrievals from TROPOMI, multi-satellite intercomparison and ground-based validation.'

We gratefully thank the reviewer for the careful reading of our manuscript and for the very constructive comments. Below, the reviewer's text is given in black while our replies and description on how the comments have been addressed in the manuscript are given in blue.

The manuscript titled '**Glyoxal tropospheric column retrievals from TROPOMI, multi-satellite intercomparison and ground-based validation**' presents a global tropospheric glyoxal product from the new TROPOspheric Monitoring Instrument (TROPOMI) along with a new retrieval algorithm that has been applied to the other satellite-based instruments for an intercomparison. These results are validated with some continental ground-based observations. The manuscript is well structured, albeit lengthy. Overall, it presents a step ahead in creating a high-resolution database for glyoxal, which is currently missing. While certain sections are well detailed and discussed, other parts are glossed over, and selective studies from the past have been used to suggest that the new product is accurate. This is especially of worry over the oceanic region where no validation is presented.

While I do not wish to be negative about the manuscript, which is worthy of publication in AMT after modifications, I hope that the authors can improve on the current draft according to the comments below.

Major comments:

Two major changes are suggested to make the paper easier to read and to highlight the capabilities and shortcomings of the updated retrieval algorithm.

1) A comparison of the different satellite products does not offer much to the current paper. All the satellite products are generated using essentially the same DOAS settings in the updated BIRA-IASB retrieval algorithm. The high level of consistency is not surprising, considering that the products are analyzed in almost the same way. The small differences that arise because of the physical detectors, footprints, etc., are not unexpected and hence the amount of discussion on this does not seem justified. It makes the paper lengthier than necessary and does not give extra useful information.

We respectfully disagree with this comment. It is true that, from a theoretical point of view, it is not surprising to have a good consistency between different satellites when common retrieval settings are applied. In practice, the low glyoxal optical depth makes it sensitive to any distortion of the measured spectra and having limited discontinuities is not necessarily as straightforward as one could think. For example, Alvarado et al. (2014) identified systematic differences when comparing different satellites, which needed further investigation. To our knowledge, this is the first study reporting satellite timeseries with this level of consistency In addition, the section also discusses the stability of the GOME-2/OMI data sets which may be impacted by the instrumental degradation. Therefore, we think it's worth insisting on this, and to demonstrate that those different data sets can be used combined together, which is very relevant for the creation of climate data records. In addition, this section gives the opportunity to discuss the spatial and natural variability of the glyoxal column fields, which is useful for glyoxal non-experts.

2) One of the highlights, which needs to be discussed in more detail, is the high CHOCHO VCDs observed over the ocean. The new product shows high values over the oceans, for which the peak is about half as much as the continental peaks. As the authors have mentioned, this is not explicable by the current known chemistry and sources. Indeed, even in highly productive waters, glyoxal and methylglyoxal are significantly undersaturated, and hence a direct source is not likely (Zhu and Kieber, 2019). Eddy covariance based observations show that the ocean surface is a sink for glyoxal for most of the day (Coburn et al., 2014).

This elevated column over the tropical oceans was reported earlier for satellite observations (Lerot et al., 2010; Vrekoussis et al., 2010) and other older papers using SCHIAMACHY. However, only one group has reported high CHOCHO over one single region in the pacific when using ground-based, or aircraft-based observations (Sinreich et al., 2010) – it has not been seen by others, even in the same region.

The largest collection of ship and land-based observations using data from nine campaigns all over the marine environment have shown that CHOCHO is mostly below the detection limit in the open ocean environment (Mahajan et al., 2014). A pattern of a significant increase in the tropics was not seen. A similar result was also seen by a more recent study by (Behrens et al., 2019) which showed that CHOCHO was mostly below the detection limit with just two days of values just above the detection limit – with the geographical distribution not the same as the new satellite product. Indeed, remote ocean observations from outside the tropical region also show similar glyoxal levels as the tropical regions (Lawson et al., 2015).

Considering this, it would be helpful to have a section about the potential interferences over the ocean:

- What was the effect of the liquid water absorption and vibration Raman infilling of Fraunhofer lines in spectral retrieval over different regions? Are oceanic regions more sensitive than over land?
- How sensitive is the retrieval over the oceans to the chosen background?
- Are there reasons why the retrieval shows significant seasonal changes over the land but not over the ocean?
- Considering the scale of the TropOMI pixels, large lakes could be used as testbeds to check the algorithm's sensitivity to water reflectance-related issues.

Some of these issues, especially related to the liquid water path, can play a big role in false positives over the tropical oceans. A study using OMI has detailed this in the past and should be referred to (Chan Miller et al., 2014) when discussing the retrieval over remote oceans. They were able to correct the elevated retrievals to large degree.

We agree that the oceanic pattern should be discussed a bit more thoroughly and we thank the reviewer for raising this point and for the different ideas and references. We also agree that the origin of this pattern is under debate and that (at least part of) it might originate from spectral interferences. We took the different comments into account for revising the manuscript. Below is first a reply to each of them and we describe after how this has been included in the text.

The fit of the liquid water signature is mostly important in remote clear oceans where the light penetration depth in ocean is the most important (see Lerot et al, 2010, Chan Miller et al., 2014, Peters et al., 2014; doi:10.5194/amt-7-4203-2014). VRS also produces a signal in those remote oceans (Vasilkov et al., 2002; https://doi.org/10.1029/2002GL014955). Peters et al. (2014) have shown that the fit of the liquid water cross-section combined with an intensity offset efficiently correct for those effects. When not corrected for, they lead to negative glyoxal columns. In our product, we see that the presence of systematically negative columns over those areas is largely limited. Over equatorial oceanic columns where enhanced glyoxal columns are observed, the liquid water/VRS signal is low. There is therefore no clear link between the liquid water path and the enhanced columns.

Uncertainties in water vapour absorption cross-section, on the other hand, might lead to spectral interferences with glyoxal and explain part of the observed signal. Sensitivity of glyoxal columns to the choice of the water vapour cross-section and of the temperature to generate it is non-negligible. When conducting sensitivity tests, we have indeed noticed that using a lower temperature similarly to what Chan Miller et al. (2014) did (i.e. 280 K) leads a reduction of the glyoxal columns for areas with high H2O content, including equatorial oceanic oceans. However, effective H2O temperatures (computed as the mean of the ECMWF T° profiles weighted by H2O concentrations) are typically larger than 290K) in area with large H2O concentrations. For this reason, we decided to continue working with the higher temperature of 293K, which appears closer to the physical conditions. These sensitivity tests nevertheless point to a need for improved water vapour absorption data.

The suggestion made by the reviewer (1st minor comment) is interesting. Introducing such a (5-10 nm) gap would remove a large part of the second glyoxal absorption band and undoubtedly would require an extension of the fitting window towards the UV to maintain stable retrievals and limit the associated noise increase. In our work, we decided to stick to our original window since it showed good performance in the past (and in the work from other teams). It also avoids the intense lines of the Ring signal below 435 nm, which may also bias the glyoxal fits. Provided this important debate, it will however worth in future to further investigate this suggestion.

The retrieval algorithm is relatively insensitive to the choice of the reference sector. The equatorial Pacific is used for both computing the mean radiance used as the reference in the DOAS fit and for the destriping step in the background correction. This ensures that any systematic row-dependent bias which would be introduced by the reference mean radiances would be efficiently removed with the destriping. In addition, the final offset correction in the background correction is based on a large range of latitudes in the Pacific covering regions with low glyoxal columns. This stabilizes in time the overall background of the columns and avoids that the possible variability in the equatorial oceanic regions impacts significantly the product. There is obviously an uncertainty associated to the chosen reference value for the background normalization as discussed and included in the error budget (section 3.4.3.). The latter is as significant as the errors due to AMF or DOAS fits. In addition, all the intermediate variables for computing the glyoxal tropospheric vertical column are given in the product (SCD, AMF, corrected-SCD). An advanced user is then in position to recompute glyoxal VCDs using a different reference background value.

Regarding the inner lakes, the TROPOMI spatial resolution allows indeed to see details unidentified with previous instruments. As discussed at the end of section 4.2.2, the sensitivity to the surface is larger in the visible than in the UV, which makes the retrieval more sensitive to ground surface signatures. Inner lakes have sometimes specific water characteristics with an associated specific "surface signature", which cannot be easily considered in our retrievals. This may impact the retrieved glyoxal columns which are sometimes high or low biased over such inner lakes. We illustrated this in the text with the example of the Kara-Bogaz-Gol near the Caspian sea, one of the saltiest lake in the world,over which enhanced glyoxal columns are measured. Other lakes show a negative signal (e.g. the Van Lake in Turkey). Those lakes are therefore unique case studies but their specificities prevent to use them as test cases easily generalizable to the oceans.

Corrections in the manuscript:

1. We have added one section 4.2.3 "Glyoxal over equatorial oceans "as suggested by the reviewer to further discuss the oceanic glyoxal pattern seen in our data sets and the apparent inconsistency with field data:

   "*A persistent equatorial oceanic glyoxal signal is seen consistently by the four sensors. The origin and the magnitude of the enhanced glyoxal concentrations over oceans remains nevertheless unclear. A similar feature has been observed from space in previous studies (Lerot et al., 2010; Vrekoussis et al., 2009; Wittrock et al., 2006), while it was much less pronounced in others (Alvarado et al., 2014; Chan Miller et al., 2014). Over the past years, glyoxal measurements have been realized with ship-borne MAX-DOAS. While Sinreich et al. (2010) measured glyoxal concentrations up to 100 ppt in the marine boundary layer of the Equatorial Pacific Ocean, most other studies (Behrens et al., 2019b; Lawson et al., 2015; Mahajan et al., 2014; Volkamer et al., 2015) reported lower concentrations inconsistent with the satellite elevated glyoxal columns. However, Volkamer et al. (2015) also reported elevated glyoxal concentrations measured with an airborne MAX-DOAS in the free troposphere, which might explain the larger satellite glyoxal signal. Remaining spectral interferences may also contribute, at least partly, to this signal. In particular, its spatial correlation with high water vapour concentration regions and the high sensitivity of glyoxal retrievals to the water vapour cross-section as discussed in section 3.1 and by Chan Miller et al. (2014) call for a careful assessment of any future new data release or for future investigation on fit strategy to mitigate this interference (e.g. Kluge et al., 2020).*"

   In the conclusions, we have also added a few sentences summarizing the issue:

   "*Although consistently identified in our four satellite data sets, the origin of the glyoxal oceanic signal remains unclear. There appears to be an inconsistency between what is measured from space and most glyoxal concentration measurements conducted in marine boundary layer campaigns. Non-negligible glyoxal concentrations in the free troposphere as measured during one campaign (Volkamer et al., 2015) might reconcile the satellite and field data. On the other hand, part of this signal may also be partly caused by remaining spectral interferences (e.g. with water vapour).*"

2. In section 3.1 on the DOAS spectral fit, the sensitivity of the CHOCHO SCDs to H2O cross-section is discussed and the choice of the temperature to generate it justified. Some statements on the impact of VRS and the reference to Peters et al. (2014) have also been added.

"*Note that the water vapour cross-section has been generated for a temperature of 293K and a pressure of 1013hPa using the HITRAN2012 database (Rothman et al., 2013) as we found that the latest HITRAN2016 version (Gordon et al., 2017) led to poorer fit quality. Sensitivity tests have shown that the retrieved glyoxal SCDs are significantly impacted by the choice of the H2O cross-section but also of its temperature. Effective water vapour temperatures (computed as the mean of temperature profiles weighted by typical H2O concentration profiles) are generally close to our selected value in regions with high water vapour content. This high sensitivity nevertheless points to the importance of having accurate water vapour cross-section, especially in regards of its possible influence on glyoxal fields over oceans (Chan Miller et al., 2014) (see section 4.2.3).*"

"*Vibrational Raman scattering on remote ocean water also introduces some spectral structures caused by the filling-in of Fraunhofer lines. However, (Peters et al., 2014) have shown the simultaneous fit of the liquid water cross-section and of an intensity offset (see below) efficiently considers all remote ocean-related structures."*

3. We have also discussed a bit more thoroughly the uncertainty related to the choice of the reference Pacific glyoxal VCD value in section 3.3 and 3.4.3. We have also added a figure in section 3.4.4 showing for one orbit the total systematic error and its different components. It shows that the background correction-related error contributes to the total error as much as the other errors.

   New text in section 3.3:

   "*There is nevertheless an uncertainty related to this reference value, which impacts the overall level of the product. This error component is further discussed in section 3.4.3 and is taken into account to estimate the total glyoxal VCD error. As all intermediate variables (SCD, corrected-SCD, AMF) are provided in the product, a user could recompute glyoxal VCDs using a different reference Pacific value."*

   New Text and figure in section 3.4.4:

   "Figure 1 shows the zonally averaged total systematic error along with its different components for one S5p orbit passing over Africa. In general, the three components contribute similarly to the total error for emission conditions. On contrary, the AMF error becomes smaller in background conditions while the two other terms dominate."

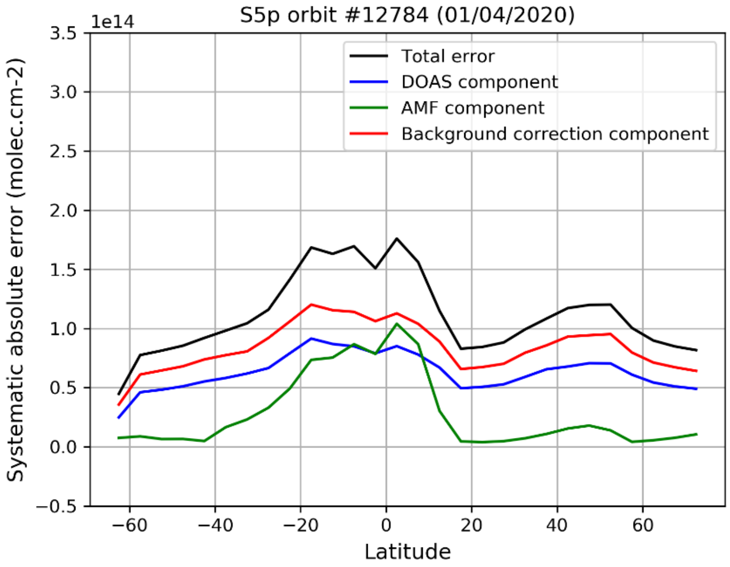

Figure 1 : Zonal mean of the total glyoxal VCD systematic error along with its different components for one single S5p orbit passing over Africa on April, 1st 2020.

Minor comments:

1. P:5, L:157-159: Authors have used 435-460 nm wavelength window for the CHOCHO retrieval. Although several groups have used this window, it can be affected by the strong water vapor absorption in this region. Have authors considered introducing a gap in the analysis window for H_2O or tried using a larger window (some studies recommend the 410-460 nm, 400-60 nm, etc.) to check the sensitivity of the retrievals?

   Please see response above.

2. The authors mention that 'There are however two stations (Phimai/Thailand and Pantnagar/India) where the satellite/MAX-DOAS bias is more significant, despite an excellent agreement between the seasonal variations. The origin of this bias is not fully understood, but it is not uncommon to have such biases in UV-Visible satellite retrievals for strongly polluted sites.' – this needs to be explored in more detail – the explanation about high pollution does not check out as the match is better at other polluted stations like Xianghe/China and Mohali/India.

   The satellite glyoxal columns at those stations are indeed in the same range as some other stations (e.g. Xianghe), but the columns as seen by the MAX-DOAS instrument are significantly larger, especially in Pantnagar but also in Phimai during the first part of the year. We have already discussed the possible causes for this bias in the text, including a possible contribution from the MAX-DOAS themselves (lines 797-802; 833-843). In the conclusions, we have slightly rephrased the sentence mentioned by the reviewer as:

   “*There are however two stations (Phimai/Thailand and Pantnagar/India) where the satellite/MAX-DOAS bias is more significant, despite a reasonable agreement of the measured seasonal variations. Although the origin of this bias is not fully* *understood, the MAX-DOAS columns at those stations are very high and it is not uncommon to have such biases in UV-Visible satellite retrievals for strongly polluted sites. It cannot be excluded that part of the bias originates from the MAX-DOAS retrieval strategy at those sites.*”

3. Line 1274: Reference title is incomplete.

   This has been corrected

4. The authors use 'excellent' at several places – this is very subjective and in most matches are not even 'great' – please reduce the use of superlatives throughout the manuscript.

   Agreed. We have softened a bit the wording.

5. The font size in most figures is too small to read without zooming.

   We have improved the visibility of Figs. 3, 11, 12, 14, 15, 16, S1, S2, S3, S4.

6. Figure 15: The legends can be moved to the empty panel.

   We think it is clearer if each row has its own legend to show clearly that they correspond to the different satellites. The legend in the upper row has however been modified to avoid crossing the axis.

7. The ground-based instruments use different DOAS retrieval settings and algorithms. For consistency and standardized validation, should they not be analyzed with the same settings and algorithms?

   Ideally, it would be indeed much better to have MAX-DOAS data retrieved in a homogeneous way. The MAX-DOAS data sets have been provided by different teams and homogenizing and reprocessing them would require a major effort, which is out of the scope of this work. However, we stated in different places in the manuscript that it would be beneficial to dedicate some resources to such an activity in future.

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