GLYoxal Retrievals from TROPOMI (GLYRETRO)

S5p+I - Validation Report (VR)

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1 Purpose and objective

The purpose of this document is to describe the validation operations of the CHOCHO S5P+I Level-2 product. This report includes details of all validation activities performed based on ground-based data as well as on data from other satellite sensors, description of their settings and main differences to GLYRETRO.

2 Document overview

3 References, Acronyms and Abbreviations

References

[RD01] Sentinel-5 Level-2 Prototype Processor Development Requirements Specification; 
  source: ESA; ref: S5-RS-ESA-GR-0131; issue: 1.7; date: 2018-06-29.

[RD02] Copernicus Sentinels 4 and 5 Mission Requirements Traceability Document (MRTD);
  source: ESA; ref: EOP-SM/2413/BV-bv; issue: 2.0 date: 2017-07-07.

[RD03] Sentinel-4 L2 Processor Component Development–Project Management Plan, 

[RD04] S5L2PP: Record of agreements from negotiation; 
  source: S5L2PP proposal consortium; ref: ST-ESA-S5L2PP-NOT-003; Issue: 1.1; date: 2016-09-02.
Acronyms and abbreviations

AMF: Air mass factor

BIRA-IASB: Royal Belgian Institute for Space Aeronomy

CHOCHO: Glyoxal

GLYRETRO: GLYoxal Retrievals from TROPOMI

MAX-DOAS: Multi-Axis DOAS

IUP: Institute of Environmental Physics

OMI: Ozone Monitoring Instrument

TROPOMI: Tropospheric Monitoring Instrument

S5P: Sentinel-5 Precursors
4 Product requirements

Requirements have been defined for a series of key species, including particulate matter, ozone, NO2, CO, SO2 and HCHO. Since it has been generally considered as a second priority, no requirement on the glyoxal column uncertainty has been defined in the S4/5 MRTD [RD02]. For the requirements on horizontal resolution and revisit time, we can use those defined for the formaldehyde columns, as those two species are useful for similar applications. The spatial requirement for HCHO has been set to 5/20 km (goal/threshold) for air quality applications and relaxed to 10/50 km for climate applications. The revisit time requirement is 0.5/2 hours for air quality applications and can obviously not be met for space instruments boarded on LEO platforms such as TROPOMI. On contrary, the future Sentinel-4 instrument aboard a geostationary platform will provide a one-hour revisit time.

Unlike for TROPOMI, glyoxal is part of the initial list of core operational products for Sentinel-4 and -5. In this context, requirements on this product have also been defined [RD01] [RD03] [RD04] and are given in Table 1. While one single total uncertainty requirement is defined for Sentinel-4, two separate values are defined for the random and systematic components of the uncertainty in Sentinel-5.

Table 1: Uncertainty Requirements on glyoxal column retrievals defined for the Sentinel-4 and -5 missions.

<table>
<thead>
<tr>
<th></th>
<th>Uncertainty (Threshold)</th>
<th>Conditions</th>
</tr>
</thead>
</table>
| Sentinel-4 | 7 x 10^{14} molec.cm^{-2} or 50% (least stringent) | SZA < 60°  
VZA < 60°  
cloud fraction < 20%  
VCD > 5 x 10^{14} molec.cm^{-2} |
| Sentinel-5 | Random error: < 1.5 x 10^{15} molec.cm^{-2}  
Systematic error: < 2.5 x 10^{14} molec.cm^{-2} or 50% (least stringent) | SZA < 70°  
VZA < 70° |
5 Reference measurements

5.1 Ground based monitoring network
Several data sets are used in this study as glyoxal reference. All the instruments for which data was available are listed in Table 1 with their respective locations. Those data sets are derived from MAX-DOAS measurements from the ground, which mainly provide tropospheric vertical column density and also offer a potential to gain information on the vertical distribution. Figure 1 shows the geographical distribution of these data sets, which are mainly located over Europe and Asia.

Table 5-1. Independent MAX-DOAS measurements used in the validation of GLYRETRO.

<table>
<thead>
<tr>
<th>Id</th>
<th>Location</th>
<th>Measurement Period</th>
<th>Type</th>
<th>Data Provider</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xi</td>
<td>Xianghe (China)</td>
<td>2008-present</td>
<td>MAX-DOAS</td>
<td>BIRA-IASB</td>
</tr>
<tr>
<td>Bej</td>
<td>Beijing (China)</td>
<td>2018-present</td>
<td>MAX-DOAS</td>
<td>USTC</td>
</tr>
<tr>
<td>Br</td>
<td>Bremen (Germany)</td>
<td>2018-present</td>
<td>MAX-DOAS</td>
<td>IUP-Bremen</td>
</tr>
<tr>
<td>Ath</td>
<td>Athens (Greece)</td>
<td>2018-present</td>
<td>MAX-DOAS</td>
<td>IUP-Bremen</td>
</tr>
<tr>
<td>Vi</td>
<td>Vienna (Austria)</td>
<td>2018-present</td>
<td>MAX-DOAS</td>
<td>IUP-Bremen</td>
</tr>
<tr>
<td>Chi</td>
<td>Chiba (Japan)</td>
<td>2018-present</td>
<td>MAX-DOAS</td>
<td>CEReS * <a href="http://atmos3.cr.chiba-u.jp/skynet/">http://atmos3.cr.chiba-u.jp/skynet/</a></td>
</tr>
<tr>
<td>Pant</td>
<td>Pantnagar (India)</td>
<td>2017-present</td>
<td>MAX-DOAS</td>
<td>CEReS * <a href="http://atmos3.cr.chiba-u.jp/skynet/">http://atmos3.cr.chiba-u.jp/skynet/</a></td>
</tr>
<tr>
<td>Phi</td>
<td>Phimai (Thailand)</td>
<td>2015-present</td>
<td>MAX-DOAS</td>
<td>CEReS * <a href="http://atmos3.cr.chiba-u.jp/skynet/">http://atmos3.cr.chiba-u.jp/skynet/</a></td>
</tr>
</tbody>
</table>
Figure 5-1: S5p Glyoxal global map retrieved using the GLYRETRO with the geographical locations of the MAX-DOAS measurements over Europe and Asia used in the validation.

5.2 Satellite measurements and Modeling support

Inter-satellite comparisons of glyoxal products are also important to assess their consistency and to verify that they can be combined together for specific studies (e.g. long-term trend analysis). Two types of comparison are performed and provide complementary information:

- Comparisons with the BIRA-IASB OMI glyoxal product generated with a similar algorithm as that applied to TROPOMI provide information on possible differences related to instrumental characteristics.

- Comparison with the IUP-Bremen TROPOMI (Alvarado et al., 2014, 2019) will be done later during the project and will allow assessing the agreement at different levels of the algorithms (e.g. SCD, offset corrections, AMF, VCDs).
In addition, comparing the TROPOMI product with glyoxal columns simulated with a
CTM in different regions worldwide may support the evaluation of the geophysical
soundness of the generated TROPOMI product, even if differences are expected given the
large uncertainties in our knowledge of the glyoxal production and destruction
mechanisms.

6 Validation approach

The GLYRETRO algorithm for the retrieval of CHOCHO is defined by BIRA-IASB. This
algorithm is tested by independent satellite and ground-based data sets based on
retrievals in similar spectral regions. Both the GLYRETRO and the MAX-DOAS
algorithms are based on the well-established DOAS method (Platt and Stutz, 2008) and
inherit from more than a decade of ground based and satellite retrievals (Alvarado et al.,
2019, 2014; Lerot et al., 2010; Vrekoussis et al., 2009, 2010; Sienreich et al., 2007, 2010;
Wittrock et al., 2006). As all current satellite glyoxal column retrievals, the GLYRETRO
algorithm consists of three elementary steps:

1. The spectral retrieval of slant column densities (SCD), which are the number
density of an absorber integrated along the light path.

2. As CHOCHO retrievals are known to suffer from offsets (satellite only), often a
semi-empirical bias correction is applied, for example by subtracting CHOCHO
columns from a region over the Pacific or over the Sahara where low CHOCHO
values are expected. If necessary, this bias correction can also be combined with a
destriping step.

3. Calculation of air mass factors (AMF) in radiative transfer simulations to convert
the retrieved SCD to vertical columns (VCD), which correspond to absorber
amounts integrated along the vertical and are independent of the light path.
Optionally, this step also includes treatment of clouds.

All these steps have associated uncertainties that arise from the technical implementation
of the algorithm, and uncertainties on parameters describing the atmospheric state. The
uncertainties related to a priori data on the atmospheric state can be assessed by comparing the TROPOMI CHOCHO VCD with independent products from other satellite sensors (e.g. OMI, GOME-2) and from ground-based instruments. In the following, preliminary results of GLYRETRO glyoxal columns are compared against MAX-DOAS data as well as against OMI and model data (MAGRITTE 2018). The investigation starts with a sensitivity test study performed to select optimal retrieval settings for ground-based data. Subsequently a comparison with available MAX-DOAS data is performed for the full period of S5P satellite measurements and finally a preliminary comparison against OMI and MAGRITTE data is presented.

6.1 Comparison with ground-based measurements.

6.1.1 Revisiting the glyoxal retrieval from ground-based data

During the last two decades, many efforts have been taken to improve the retrieval of weaker absorbers such as CHOCHO. However, the uncertainties are still large in comparison to strong absorbers such as NO₂. Various algorithms and definitions of parameters used in CHOCHO retrievals are still in use, sometimes showing consistent results but sometimes also large differences, depending on the wavelength window, polynomial and cross-sections of interfering species included in the retrieval. Therefore, we briefly revisit the CHOCHO retrieval in order to find the optimal parameters, based on sensitivity studies as described below.

For this glyoxal sensitivity study, measurements performed in Athens were used. A systematic variation of parameters has been performed to find the optimal parameter set for CHOCHO. The parameters evaluated were the cross-sections included in the retrieval, the fitting window, and the polynomial degree.

- **Start wavelength**: 410 nm to 440 nm.
- **End wavelength**: 442 nm to 472 nm.
- **Cross-sections**: CHOCHO (Volkamer et al., 2005; 296 K), NO₂ (Vandaele et al., 1998; 220 K and 294 K), O₃ (Thalmann et al., 2013; 293 K), O₃ (Serduchenko et al., 2014), H₂O (Rothman et al., 2013), Ring calculated by SCIATRAN model (Vountas et al., 1998).

- **Number of polynomial coefficients**: 3 to 6.

Every combination of parameters was applied to more than 30 measurements per day at two elevation angles (2° and 30°) and using the zenith measurement closest in time as reference spectrum. In order to compensate possible straylight effects, a constant intensity offset was applied.

Figure 6-1 shows the mean root mean square (RMS) obtained in the glyoxal retrievals computed for all possible combinations of start and end wavelengths for each combination of cross-sections and polynomial degrees. The mean RMS decreases with increasing number of cross-sections, however this decrease is more significant when stronger absorbers are included in the fit, the most significant reduction being achieved by adding water vapour especially for 2° elevation. In addition, including a high temperature NO₂ cross-section leads to a reduction of mean RMS, by accounting for the tropospheric contribution in the region of study. In addition, a polynomial with 6 coefficients leads to lower RMS, however no significant difference is observed between the results for polynomial degree 5 and 6.
Figure 6-1: The mean RMS for glyoxal retrievals with their respective standard deviation as error bar computed over all possible fitting windows for each combination of cross-sections and different polynomials (colour bars) for measurements performed in Athens on 6 August 2018, elevation angle of 2° and 30° at an azimuth direction of 52.5° (S direction).

For the selection of fitting window, RMS, fit error, and SCD are evaluated as function of start and end limits of wavelength intervals at steps of 0.5 nm. These limits cover the most representative absorption bands of glyoxal. Figure 6-2 (a, b, c) shows the dependency of glyoxal retrievals on wavelength window for fit error, RMS and SCD at an elevation angle of 2° and azimuth viewing direction of 52.4° (S direction). Figure 6-2a shows the variability of fit error with wavelength, where red boxes denote the fit windows with lower fit errors; however regions that do not include the strongest absorption band of glyoxal are excluded. The lowest fit errors correspond to the interval with start wavelengths from 433 to 437.5 nm, and end wavelengths from 464 to 471 nm. This fit window is also within the intervals where the lower RMS is found (see Figure 6-2b, green boxes), the lowest RMS corresponding to intervals with start wavelengths from 433 to 440 nm and end wavelengths from 456 to 472 nm. For the SCDs some fit intervals show large variability (see Figure 6-2c, blue boxes). Only those fit windows with homogenous variability are selected and regions that do not contain the strongest absorption band of glyoxal are excluded. Thus, any fit window combination contained in the range with start wavelengths from 433 to 437.5 nm and end wavelengths from 464 to 472 is suitable for a good glyoxal retrieval considering the fact that these combinations also correspond to low fit error and RMS. The lowest error corresponds to a fit window from 436 to 468 nm (polynomial with 6 coefficients).
Figure 6-2: Colour mapping of a) fit errors, b) RMS, and c) SCD of CHOCHO for different wavelength windows with start limits of 410–440 nm and end limits of 442–472 nm for measurements performed at 2° elevation angle and an azimuth direction of 52.5° (S direction) over Athens on 6 August 2018.

In the following, retrievals using the parameters resulting from the sensitivity tests (Fit A) are compared to results obtained with the GLYRETRO (Fit C) and IUP S5P Glyoxal (Fit B) fit settings. These settings are summarized in the Table 6-1.

Figure 6-3 shows time series of CHOCHO SCD (a), fit error (b), and RMS (c) retrieved using three different settings (optimal – Fit A, IUP S5P Glyoxal – Fit B, GLYRETRO – Fit C). The SCDs are compared for elevation angles of 2° and 30°. The three retrievals show a similar temporal evolution with almost no difference among the SCDs. However, the retrieval using the optimal settings has the lowest error and an improvement of about 5% against the other two fits (see Figure 6-3b). A similar behaviour is observed in the comparison of RMS (see Figure 6-3c) but a lesser degree.

Thus, this optimal fit will be applied to MAX-DOAS measurements performed in Athens, Vienna, Bremen, and Xianghe.
Table 6-1. DOAS settings for optimal retrieval (Fit A), IUP S5P (Fit B), and GLYRETRO (Fit C) applied to MAX-DOAS measurement from Athens.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Fit A</th>
<th>Fit B</th>
<th>Fit C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fitting window</td>
<td>436-468 nm</td>
<td>433-465 nm</td>
<td>435-460 nm</td>
</tr>
<tr>
<td>Polynomial</td>
<td>6 coefficients</td>
<td>5 coefficients</td>
<td>4 coefficients</td>
</tr>
<tr>
<td>Cross-sections used:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHOCHO (Volkamer et al., 2005)</td>
<td>Yes (296 K)</td>
<td>Yes (296 K)</td>
<td>Yes (296 K)</td>
</tr>
<tr>
<td>NO₂ (Vandaele et al., 1998)</td>
<td>Yes (220K, 294 K)</td>
<td>Yes (220K, 294 K)</td>
<td>Yes (220K, 294 K)</td>
</tr>
<tr>
<td>O₃ (Thalman et al., 2013)</td>
<td>Yes (293 K)</td>
<td>Yes (293 K)</td>
<td>Yes (293 K)</td>
</tr>
<tr>
<td>O₃ (Serduchenko et al., 2014)</td>
<td>Yes (223 K)</td>
<td>Yes (223 K)</td>
<td>Yes (223 K)</td>
</tr>
<tr>
<td>H₂O (Rothman et al., 2013)</td>
<td>Yes (296 K)</td>
<td>Yes (296 K)</td>
<td>Yes (296 K)</td>
</tr>
<tr>
<td>Ring effect</td>
<td>Ring cross section calculated by SCIATRAN model (Vountas et al., 1998)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6-3: a) Time series of CHOCHO DSCs retrieved from the MAX-DOAS measurements in Athens at elevation angles of 2° and 30° with an azimuth direction of 52.5° (S direction) for the period between 6 and 9 August 2018. Also the fit error (b) and RMS (c) for 8 August 2018 presented.
6.1.2 Results from validation using ground-based data

In order to test the accuracy of GLYRETRO, glyoxal columns are compared to reference measurements acquired by Multi-Axis-DOAS measurements from stations located in Athens, Vienna, Bremen, Xianghe, Pantnagar, Chiba, and Phimai.

6.1.2.1 Xianghe and Beijing (China)

The Xianghe and Beijing stations are located in China. The Xianghe MAX-DOAS is operated by BIRA-IASB, while the Beijing data set has been kindly provided by USTC. In Xianghe, we had the flexibility to apply the optimal settings described in section 6.1 to retrieved the slant columns, which then have been converted to VCDs using the geometrical approach. The MAX-DOAS data in Beijing have been retrieved as described in Javed et al. (2019). Only MAX-DOAS measurements in a window of 3 hours centered around the S5p overpass time have been considered, while S5p observations in a radius of 20 km from the station have been considered. In this comparison, only days with data available for both MAX-DOAS and satellite are considered. Figure 6-4 shows time series of monthly median CHOCHO columns at Xianghe and Beijing in 2018 and 2019. The general seasonal patterns as observed by TROPOMI and the MAX_DOAS are consistent with each other. The lower panels show the time series of the monthly median ground-based/satellite differences, along with the variability of the differences illustrated by the boxes and bars showing the 5th, 25th, 75th and 95th percentiles of the daily differences. In Xianghe, the monthly median differences are generally lower than 2x10^{14} molec.cm^{-2}. As indicated by the boxes, the day-to-day variability of the differences is significant. In Beijing, the spread of the differences is larger, probably due to the more extreme conditions covered. It has also to be noted that the errors associated to the MAX-DOAS data for this station are larger than that of S5P.
Figure 6-4: Time series of spatially co-located monthly median CHOCHO columns from S5p and MAX-DOAS (upper panel) and monthly median differences (lower panels) along with their day-to-day variability represented by 5th, 25th, 75th and 95th percentiles (boxes and error bars) at Xianghe and Beijing locations for 2018-2019.

6.1.2.2 Chiba and Kasuga (Japan)
The MAX-DOAS data from the Chiba and Kasuga stations in Japan are provided by Chiba University (http://atmos3.cr.chiba-u.jp/skynet/data.html). The MAX-DOAS retrieval scheme used to produce those data sets is described in Irie et al. (2011). The selection has been done for a radius of 20 km with a 2 hours overpass window and using only common days for both data sets. Like in Figure 6-4, Figure 6-5 compares the MAX-DOAS and S5p glyoxal time series in Chiba and Kasuga. However, the MAX-DOAS data sets provided by Chiba University also contain glyoxal vertical profile as retrieved by their algorithm, with concentrations given 6 different layers from 0 to 6km. The MAX-DOAS columns result from the integration of those glyoxal profiles. Having those profiles allow to apply the satellite averaging kernels to the MAX-DOAS measurements in order to account for different a priori information and sensitivity. However, this has little effect at those two stations (blue curve compared to black curve), meaning that the satellite a priori normalized profiles are close to the normalized MAX-DOAS profiles. The consistency
between the products is good with small mean biases of about $0.11\pm0.97\times10^{14}$molec.cm$^{-2}$ and $-0.38\pm0.97\times10^{14}$molec.cm$^{-2}$ for Chiba and Kasuga, respectively.

The MAX-DOAS instruments have limited sensitivity above the boundary layer, especially in case of large aerosol content (Vlemmix et al., 2011). Depending on the retrieval scheme, the MAX-DOAS profiles may be significantly contaminated by the a priori profile in case of poor sensitivity at elevated layers. The Chiba University retrieval scheme uses an approach that constraints the glyoxal concentrations in elevated layers to be a fraction of the glyoxal content in the surface layer (Irie et al., 2011). This can potentially lead to biases on the MAX-DOAS glyoxal columns in case of aerosol-polluted conditions. Even if the sites of Chiba and Kasuga are relatively clean, this motivates the comparison of the S5p columns with the MAX-DOAS 0-1km partial columns where most of the glyoxal is expected to be located (green curves). Here, the 0-1km partial columns are slightly lower than both the total MAX-DOAS columns and the S5p columns. For those unpolluted sites, the a priori information has less influence on the MAX-DOAS retrieved column/profile. Therefore, the total columns are likely more realistic. This may be different for more polluted stations like those presented in the next section.
Figure 6-5: Time series of spatially co-located monthly median CHOCHO columns from S5p and MAX-DOAS (upper panel) and monthly median differences (lower panels) along with their day-to-day variability represented by 5th, 25th, 75th and 95th percentiles (boxes and error bars) at Chiba and Kasuga locations in Japan for
2018 - 2020. S5p columns (red) are compared to original MAX-DOAS columns (black), to MAX-DOAS columns smoothed by the S5p AK (blue) and to MAX-DOAS 0-1km partial columns (green).

6.1.2.3 Pantnagar (India) and Phimai (Thailand)

Additional MAX-DOAS data are provided by Chiba University at the stations Phimai (Thailand) and Pantnagar (India), which are both regions characterized by large natural influences and fires events. The aerosol content is quite high at those sites, especially in Pantnagar where aerosol optical depths range from 0.2 to 1.5. For this comparison, S5p data has been selected within 20 km around the station and MAX-DOAS measurements within 2 hours of the satellite overpass time. Similarly to Figure 6-5, Figure 6-6 compares glyoxal columns from TROPOMI and the MAX-DOAS instruments in Pantnagar and Phimai. At those two stations, the TROPOMI glyoxal columns have a seasonal variability consistent with the MAX-DOAS observations but there is an important systematic bias, especially in Pantnagar where the mean bias is $-3.41\pm2.08\times10^{14}$ molec.cm$^{-2}$. In Phimai, it is slightly less important, but still around $-1.87\pm0.86\times10^{14}$ molec.cm$^{-2}$. Smoothing the MAX-DOAS columns with the TROPOMI averaging kernels has little effect as shown by the blue curves, to be compared to the black curves, meaning that the normalized satellite a priori profiles are quite consistent with the provided MAX-DOAS profiles. Following the discussion of the previous section, we also compared the TROPOMI columns to the MAX-DOAS 0-1km partial columns. This comparison is much better, especially in terms of absolute columns. Since those sites contain often high load of aerosols, we suspect that the MAX-DOAS sensitivity above 1 km is low, with the consequence that the provided glyoxal concentrations in elevated layers are mostly constrained to be a fraction of the surface layer measurements, which might result in a high bias in the total column. Demonstrating this would require to have MAX-DOAS averaging kernels and is beyond the scope of this study.
Figure 6-6: Time series of spatially co-located monthly median CHOCHO columns from S5p and MAX-DOAS (upper panel) and monthly median differences (lower panels) along with their day-to-day variability represented by 5th, 25th , 75th and 95th percentiles (boxes and error bars) at Pantnagar and Phimai locations in India and Thailand for 2018 – 2020. S5p columns (red) are compared to original MAX-
DOAS columns (black), to MAX-DOAS columns smoothed by the S5p AK (blue) and to MAX-DOAS 0-1km partial columns (green). The mean biases when comparing to the original MAX-DOAS columns are $3.41\pm2.08\times10^{14}$ molec.cm$^{-2}$ and $1.87\pm0.86\times10^{14}$ molec.cm$^{-2}$, for Pantnagar and Phimai, respectively.

6.1.2.4 Athens, Bremen, and Vienna (Europe)
The MAX-DOAS data from Athens, Bremen, and Vienna are part of the BREDOM network at the University of Bremen. The columns have been retrieved using the optimal settings described in the section 6.1. The vertical columns were obtained using a geometrical approach. The selection of the data is performed for a radius of 20 km around the stations and within 3 hours of the S5P overpass.

Figure 6-7 shows time series of MAX-DOAS data compared to GLYRETRO columns. The agreement for the Athens station is quite good, the data following a similar seasonal variation with a mean bias of about $0.1\times10^{14}$ molec.cm$^{-2}$. Larger differences are observed for Bremen (mean bias: $3.5\times10^{14}$ molec.cm$^{-2}$), where limited sensitivity to surface concentrations may complicate the retrieval for both (satellite and ground-based). Frequent clouds and large solar zenith angles are the main reason for these problems, in particular in winter. Further investigations will be performed in order to correlate the effects of cloud and aerosols with the low sensitivity of the retrievals (satellite and ground). The Vienna station shows some consistency between MAX-DOAS and S5P for summer time but poor agreement in the winter season. These differences could be related to the low sensitivity of satellite CHOCHO measurements during the winter season.
Figure 6-7: Time series of spatially co-located monthly median CHOCHO columns from S5p and MAX-DOAS (upper panel) and monthly median differences (lower panels) at Athens, Bremen, Vienna for 2018 – 2019. S5p columns (red) are compared to original MAX-DOAS columns (black). The mean biases when comparing to the original MAX-DOAS columns are $-0.2\pm1.0\times10^{14}\text{molec.cm}^{-2}$, $-1.8\pm2.2\times10^{14}\text{molec.cm}^{-2}$, and $-2.1\pm1.9\times10^{14}\text{molec.cm}^{-2}$ for Athens, Bremen, and Vienna, respectively.
6.1.3 Status of validation

So far the validation of the S5P TROPOMI glyoxal vertical column data is mainly based on satellite to MAX-DOAS, for which good agreement is found, but also between TROPOMI and OMI, and Model data. Validation for regions using ground based MAX-DOAS data is limited to Europe and Asia regions (Xianghe, Beijing, Pantnaga, Phimai, Athens, Bremen, Vienna, Chiba, Kasagua). However, it should be noted that for these comparisons the CHOCHO columns were over some regions where the glyoxal signal is quite low and difficult to detect from space (e.g. Bremen).

6.1.4 Bias

Based on the MAX-DOAS data sets used for this study, the mean systematic difference range from \(-3.4 \times 10^{14}\) to \(0.4 \times 10^{14}\) molec.cm\(^{-2}\), depending on the station. Note that the larger observed biases occur for stations frequently contaminated by large aerosol content. Those conditions limit the MAX-DOAS sensitivity above the boundary layer, which might lead to a high bias of the MAX-DOAS columns due to constraints applied on the a priori profile used in the retrieval scheme. For the two Chinese stations in Beijing and Xianghe, given the difficult observation conditions there (polluted scene and large solar zenith angle in winter), the mean bias is reasonable \((<1e14 \text{ molec.cm}^{-2})\), although there is a high variability in the month-to-month differences. In Europe, the consistency between TROPOMI and the MAX-DOAS data sets is also quite good, especially at moderate latitudes or during summertime. When the latitude increases, satellite/MAX-DOAS differences increase, probably due to the lower satellite sensitivity to the surface.
6.1.5 Dependence on influence quantities

As poor agreement has been found for some locations, the impact of factors such as clouds and aerosols will be investigated in order to better understand the reasons for the observed differences between CHOCHO columns from MAX-DOAS and those columns from GLYRETRO.

6.1.6 Short term variability

Overall, the figures presented before show that the short-term variability seen in the MAX-DOAS measurements is nicely reproduced by GLYRETRO. The only exception is at the higher latitudes of the European stations. Figure 6-8 presents for 4 stations correlation regression between the TROPOMI and MAX-DOAS glyoxal columns. At the exception of Pantnagar where the correlation coefficient is low (0.3), this coefficient is reasonable for other stations (from 0.5 to 0.8). Note that if we would compare the TROPOMI columns to the MAX-DOAS partial 0-1km columns, the correlation coefficients would barely change. Only the slope of the regression would increase.
Figure 6-8: Correlations plots between S5p and MAX-DOAS glyoxal columns for four example stations. The correlation coefficients vary between 0.3 and 0.83, the best correlation being found in Kasuga and the lowest in Pantnagar. Note if the TROPOMI columns are compared to the MAX-DOAS partial 0-1km columns, the correlation coefficients would barely change.

Over Europe the correlation varies according to the region, the TROPOMI and MAX-DOAS observations being in Athens high correlated, but anti-correlated in Bremen and Vienna (see Figure 6.9) mostly because of the increasing differences during wintertime. At those stations, the differences remain nevertheless small during summertime. It has to be noted that cloud contamination is also frequent at those stations, making the comparison more difficult due to possible sampling issues.
Figure 6-9: Correlations plots between S5p and MAX-DOAS glyoxal columns for three example stations in Europe. The correlation coefficients vary between -0.1 and 0.7, the best correlation being found in Athens.

6.2 Inter-satellite comparison.

6.2.1 TROPOMI inter-algorithm comparison

This section will written in the next version.
6.2.2 Inter-sensor comparison

In this section, TROPOMI glyoxal tropospheric columns are compared with OMI columns, both products being generated with the same retrieval algorithm developed by BIRA-IASB. This comparison allows identifying possible differences due to instrumental features.

Figure 6-9 compares seasonal glyoxal field maps for OMI and TROPOMI, when considering the periods 2005-2012 and June 2018-May 2020, respectively. Those maps show very similar patterns both in terms of geographic distribution of the glyoxal signal and of its amplitude. There is no clear systematic bias between those two products. The largest glyoxal columns are generally observed in Tropical regions. At mid-latitudes, glyoxal columns are generally lower but increase during summertime as a response to biogenic activity.

Glyoxal columns increase significantly during fire events. Regions with large scale fires such as Amazonia, Africa, India, Thailand have the largest glyoxal columns. The intensity of those fires may change from a year to another, which causes a significant inter-annual variability. For example, Figure 6-10 shows OMI and TROPOMI time series of glyoxal over Amazonia where intense fires take place generally in the period August-October and a maximum in the glyoxal columns is seen at this period. However, there is a large interannual variability in the number of fires and their intensity, which directly impacts the amplitude of the glyoxal peaks. The right panel of the Figure 6-10 shows a time series of estimates of fire emissions in this region and there is a 1-to-1 correspondence between years with large emissions and large observed glyoxal columns. We also see on this figure that TROPOMI nicely extends the OMI time series. Another example of this is in Souttheastern Australia where TROPOMI has seen very large glyoxal columns due to the intense fires that took place in January 2020. Due to the limited number of years in the TROPOMI time series, we see in that region larger glyoxal columns in the TROPOMI map for December-January-February compare to OMI.
Anthropogenic emissions in highly populated area may also lead to elevated glyoxal columns. Both OMI and TROPOMI detect hot spots of glyoxal over megacities like Beijing, Bangkok, Johannesburg, Mexico, New Delhi, Teheran, Sao Paulo.
Figure 6-9: Comparison of glyoxal column (× 10^14 molec.cm^-2) seasonal maps as derived from OMI (left panels) and TROPOMI (right panels) observations. Those maps have been produced by combining OMI observations from 2005 to 2012 and TROPOMI observations from June 2018 to May 2020.

Figure 6-10: Left panel: Time series of glyoxal columns in Amazonia as seen by OMI and TROPOMI. As indicated in the legend, different curves show daily, monthly and 3-months smoothed median values. Right panel: Annual emissions estimated from the Global Fire Emissions Database in Amazonia. (Figure taken from https://www.globalfiredata.org).

Figure 6-11 compares the glyoxal time series from OMI and TROPOMI in different regions worldwide covering different type of emissions. All those different time series show a very good overlap of the TROPOMI and OMI curves in 2018, indicating that the TROPOMI glyoxal measurements are very consistent with those of OMI in terms of amplitude and seasonal variations. In Tropical regions, the OMI data set is relatively stable. At higher latitudes, some strange patterns are identified. For example, the amplitude of the
seasonality abruptly changes in Europe and US in 2014. Although not entirely clear, it has been observed that the latitudinal dependence of the slant columns has changed over time with a stronger decrease at higher latitudes in winter, which might explain part of the low bias in winter for those regions. The continuously evolving row anomaly also affects likely the product. Therefore, the glyoxal changes in time observed in China and India are to be interpreted cautiously. Nevertheless, the excellent agreement between the two sensors after 14 years of operations is very encouraging. In future, some comparisons with the GOME-2A and B data sets will also be performed.

Figure 6-12 zooms in on the same regions on the TROPOMI measurement period and compares the retrieved columns with climatological values based on the entire OMI data set as well as with columns modelled the BIRA-IASB CTM MAGRITTE using emissions inventories from 2018. It clearly shows that the mean differences between the two instruments are very small (<5e13 molec.cm⁻²) and they both capture consistently similar glyoxal variations. The comparison with modelled columns also give confidence into the physical soundness of the measurements. Although there are obviously some larger differences in the absolute column numbers, the seasonal variations are very consistent, even in strongly polluted regions like China.
Figure 6-11: Time series of glyoxal columns as seen by OMI and TROPOMI in different regions worldwide. As indicated in the legend, different curves show daily, monthly and 3-months smoothed median values.
Figure 6-12: Time series of TROPOMI glyoxal columns compared with a climatology of glyoxal columns based on the entire OMI data set, and with glyoxal columns modelled with the CTM MAGRITTE using emission inventories from 2018. The red error bars indicate the estimated TROPOMI column uncertainties, while the black ones represent the OMI interannual variability.

7 Conclusions

In general, the GLYRETRO and MAX-DOAS data show a similar temporal behaviour for all stations but some differences are observed for stations with frequently cloudy scenes such as Bremen. A low mean bias is observed in general and good correlation between both data sets. The observed discrepancies could either be related to external quantities such as aerosols and clouds or to differences in the a-priori information used in the retrieval. This will be investigated in more detail in the next phase of the project.

Satellite comparisons show very consistent results between TROPOMI and OMI in terms of amplitude and seasonal variations. In Tropical regions, the OMI data set is relatively stable while some strange patterns are identified at higher latitudes after 2012. Overall, the excellent agreement between the two sensors after 14 years of operations is very encouraging. In future, some comparisons with the GOME-2A, B and C data sets will also be performed as well as against IUP S5P Glyoxal retrieval.

On the other side, the comparison with BIRA-IASB CTM MAGRITTE columns also give confidence into the physical soundness of the measurements. Although there are
obviously some larger differences in the absolute column numbers, the seasonal variations are very consistent, even in strongly polluted regions like China.

8 References


