Glyoxal tropospheric column retrievals from TROPOMI, multi-satellite intercomparison and ground-based validation

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24 Abstract. We present the first global glyoxal (CHOCHO) tropospheric column product derived from the 25 TROPOspheric Monitoring Instrument (TROPOMI) on board of the Sentinel-5 Precursor satellite. Atmospheric glyoxal results from the oxidation of other non-methane volatile organic compounds (NMVOCs) and from direct 26 27 emissions caused by combustion processes. Therefore, this product is a useful indicator of VOC emissions. It is generated with an improved version of the BIRA-IASB scientific retrieval algorithm relying on the Differential 28 29 Optical Absorption Spectroscopy (DOAS) approach. Among the algorithmic updates, the DOAS fit now includes corrections to mitigate the impact of spectral misfits caused by scene brightness inhomogeneity and strong NO_2 30 absorption. The product comes along with a full error characterization, which allows providing random and 31 32 systematic error estimates for every observation. Systematic errors– are typically in the range of $1-3x10^{14}$ 33 molec/cm² (~30-70% in emission regimes) and originate mostly from a priori data uncertainties as well as spectral 34 interferences with other absorbing species. The latter may be at the origin, at least partly, of an enhanced glyoxal signal over Equatorial Oceans and further investigation is needed to mitigate them. Random errors are larger 35 (>6x10¹⁴ molec/cm²) but can be reduced by averaging observations in space and/or time. Benefiting from a high 36 37 signal-to-noise ratio and a large number of small-size observations, TROPOMI provides glyoxal tropospheric 38 column fields with an unprecedented level of details.

- 39 Using the same retrieval algorithmic baseline, glyoxal column data sets are also generated from the Ozone
- 40 Monitoring Instrument (OMI) on Aura and from the Global Ozone Monitoring Experiment-2 (GOME-2) on board
- 41 of Metop-A and Metop-B. Those four data sets are intercompared over large-scale regions worldwide and show
- 42 a high level of consistency. The satellite glyoxal columns are also compared to glyoxal columns retrieved from
- 43 ground-based Multi-Axis (MAX-) DOAS instruments at nine stations in Asia and Europe. In general, the satellite

- 44 and MAX-DOAS instruments provide consistent glyoxal columns both in terms of absolute values and variability.
- 45 Correlation coefficients between TROPOMI and MAX-DOAS glyoxal columns range between 0.61 and 0.87.
- 46 The correlation is only poorer at one mid-latitude station, where satellite data appears low biased during
- 47 wintertime. The mean absolute glyoxal columns from satellite and MAX-DOAS generally agree well for
- 48 low/moderate columns with differences less than 1×10^{14} molec/cm². A larger bias is identified at two sites where
- 49 the MAX-DOAS columns are very large. Despite this systematic bias, the consistency of the satellite and MAX-
- 50 DOAS glyoxal seasonal variability is high.

51 **1. Introduction**

- 52 Exposure to poor air quality kills millions of people annually (e.g. Vohra et al., 2021; World Health Organization, 53 2016) due to natural and human emissions of a large range of particulate matters and gases, including among 54 others nitrous oxides (NOx), sulphur dioxide, carbon monoxide, methane and volatile organic compounds 55 (VOCs). The latter, in combination with NOx, play a significant role in the secondary production of tropospheric 56 ozone (Jacob, 2000), which is highly toxic for the respiratory system and also contributes to global warming 57 because of its absorption in the thermal infrared. Global measurements of atmospheric concentrations of the ozone 58 precursors are therefore crucial. The number of VOCs that can be found in the atmosphere is manifold, but only 59 a few of them can be probed using remote sensing techniques. For example, formaldehyde (HCHO) measurements 60 have been used in many studies as a proxy for probing emissions of non-methane VOCs of biogenic, pyrogenic and anthropogenic origin (e.g. Abbot et al., 2003; Barkley et al., 2013; Bauwens et al., 2016; Beekmann and 61 62 Vautard, 2010; Curci et al., 2010; Jin et al., 2020; Marais et al., 2012; Palmer et al., 2006; Stavrakou et al., 2016; 63 Wells et al., 2020).
- 64 With a lifetime of a few hours, glyoxal (CHOCHO) is another short-lived VOC that can be detected remotely, 65 offering the potential to provide information on Non-Methane VOC (NMVOC) emissions. Over the past few 66 years, an increasing number of studies (e.g. Cao et al., 2018; Chan Miller et al., 2017; Fu et al., 2008; Li et al., 2016; Liu et al., 2012; Stavrakou et al., 2009, 2016; Wittrock et al., 2006) have exploited glyoxal measurements 67 from space, often in combination with formaldehyde. Being produced from similar sources, those two species are 68 69 complementary as they have different production yields. For example, the oxidation of aromatics produces glyoxal 70 with a much higher yield than formaldehyde (Cao et al., 2018). Although being both mostly produced via the 71 oxidation of other VOCs, direct emissions from anthropogenic and fire activities also occur, and contribute more 72 to the glyoxal global budget than to the formaldehyde one (Stavrakou et al., 2009b, 2009a). This motivated many 73 studies to investigate the ratio of glyoxal to formaldehyde concentrations or columns as a possible metric to 74 discriminate between different types of VOC emissions (e.g. Chan Miller et al., 2014; DiGangi et al., 2012; Hoque 75 et al., 2018; Kaiser et al., 2015; Vrekoussis et al., 2010). Glyoxal measurements are also essential for establishing 76 the global budget of secondary organic aerosols (SOAs). Indeed, with a high solubility in water, glyoxal undergoes 77 heterogeneous uptake on aerosols and cloud droplets where the subsequent aqueous-phase chemistry forms SOA 78 (Chan et al., 2010; Fu et al., 2008; Hallquist et al., 2009; Knote et al., 2014; Li et al., 2016; Volkamer et al., 2007).
- Glyoxal has three absorption bands in the visible spectral range that have been exploited to remotely retrieve information on its atmospheric abundance using the Differential Optical Absorption Spectroscopy method (DOAS, Platt and Stutz, 2008) applied to ground-based (e.g. Benavent et al., 2019; Hoque et al., 2018; Javed et

82 al., 2019; Schreier et al., 2020), air-borne (e.g. Kluge et al., 2020; Volkamer et al., 2015), ship-borne (e.g. Behrens 83 et al., 2019; Sinreich et al., 2010) and space-based instruments. The first global glyoxal tropospheric column 84 observations from space have been realized by Wittrock et al. (2006) using nadir measurements from the 85 SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY) instrument. Based 86 on this pioneering work, different glyoxal data products were derived from the Global Ozone Monitoring 87 Experiment-2 (GOME-2) (Lerot et al., 2010; Vrekoussis et al., 2009) and from the Ozone Monitoring Instrument 88 (OMI) (Alvarado et al., 2014; Chan Miller et al., 2014). All those different products rely on a similar DOAS 89 approach, but generally differ from each other by the choice of the fit settings and of the auxiliary input data.

90 In general, the glyoxal optical depth is very low (< 5e-4), typically one order of magnitude smaller than the NO₂ 91 optical depth in the same spectral range. This results in retrievals prone-to-noise, requiring to average many of 92 them to extract meaningful glyoxal signals. With an enhanced spatial resolution resulting in a number of 93 observations more than ten times larger than provided by its predecessor OMI, the TROPOspheric Monitoring 94 Instrument (TROPOMI), operating since 2017, allows observing weak atmospheric absorbers with an 95 unprecedented level of spatio-temporal details. This has been illustrated by Alvarado et al. (2020a) who 96 investigated the large amounts of formaldehyde and glyoxal emitted by the intense North-American wildfires in 97 August 2018 as observed by TROPOMI for several days and over long distances. Theys et al. (2020) have 98 evaluated the respective contributions to the hydroxyl radical production in fresh fire plumes from nitrous acid, 99 VOCs and other sources with the support of different TROPOMI data sets, including the glyoxal data product 100 described here.

This work presents the latest version of the BIRA-IASB scientific glyoxal tropospheric column retrieval algorithm that has been applied to three years of TROPOMI measurements, and also to data from the predecessor nadir instruments OMI and GOME-2A/B. The quality of the TROPOMI glyoxal retrievals is investigated with (1) a global intercomparison of the satellite glyoxal data products generated with a common algorithm and (2) comparisons with independent glyoxal measurements from a series of Multi-AXis DOAS (MAX-DOAS) instruments located at nine stations in Asia and Europe.

After a brief introduction of the satellite instruments used in this study in Section 2, the retrieval algorithm and its different steps are described in Section 3, with emphasis on the updated and innovative aspects compared to heritage studies. This section also presents the typical random and systematic errors associated to the retrievals and how they are estimated for each individual measurement. Section 4 presents the evaluation of the inter-satellite consistency by comparing both seasonal global spatial patterns as seen from different instruments as well as monthly mean time series and seasonal cycles in a series of selected large-scale regions. Finally, Section 5 presents validation results based on MAX-DOAS data.

114 2. TROPOMI and other nadir-viewing satellite sensors

115 TROPOMI was launched on 13 October 2017 on board of the Sentinel-5 precursor platform. It flies on a sun-116 synchronous Low Earth Orbit (LEO) with an ascending node crossing the equator at the local time of 13:30. In 117 the series of Sentinel missions from the European Union Copernicus programme, it is the first one dedicated to 118 atmospheric composition. The instrument operates in a nadir viewing mode and measures Earthshine radiances

and solar irradiances in the ultraviolet (UV), visible, near infrared and short infrared spectral bands. It aims at

- 120 providing column amounts of a number of key pollutants, such as ozone (O₃), NO₂, SO₂, HCHO, CO, CH₄ as well
- as cloud and aerosol parameters. TROPOMI offers a quasi-daily global coverage at the unprecedented spatial
- resolution of 3.5x5.5 km² (3.5x7 km² before August 2019) in the UV-visible spectral range. It is an imager-type
- 123 instrument using a two-dimensional Charge Coupled Device (CCD) for the light measurements, the detector
- columns being used for the spectral resolution while the rows are binned to resolve spatially the 2600 km across-
- track swath into 450 individual ground pixels. The spectral resolution of the instrument is about 0.5 nm and offers
 a remarkably high signal-to-noise ratio of about 1500 in band 4 (405-500 nm) used in this study. More details on
- 127 the instrument and its performance can be found in (Kleipool et al., 2018; Ludewig et al., 2020; Schenkeveld et
- 128 al., 2017; Veefkind et al., 2012). The TROPOMI measurements allow to derive the vertical columns of multiple
- species, some of them not included among the operational products listed above. Glyoxal is one of them and the
- 130 details on how its column quantities are retrieved will be described in the next section.

The TROPOMI design strongly inherits from past nadir-viewing sensors, and in particular from the Ozone 131 132 Monitoring Instrument (OMI) that we use to evaluate the TROPOMI glyoxal product presented in this work. OMI 133 (Levelt et al., 2006) is also an imager instrument and flies on an early afternoon orbit since October 2004. The 134 OMI swath, divided into 60 across-track pixels with a size varying from 13x24 km² (at nadir) to 13x150km² (at 135 the edges), allowed a daily global coverage before being limited in 2008 by the so-called row anomaly. The latter 136 consists in a modification of the signal recorded by OMI at specific rows, due to a mechanical obstruction of the 137 field of view, and leads to lower quality spectral measurements (Torres et al., 2018). We also exploit spectral measurements from the Global Ozone Monitoring Experiment-2 (GOME-2) instruments aboard the Metop-A and 138 139 Metop-B platforms. In contrast to OMI and TROPOMI, the GOME-2 instruments (Munro et al., 2016) fly on 140 early morning LEOs with local equator crossing times around 09:30 and are scanning spectrometers, meaning that 141 across-track pixels are successively sounded. The scan is divided into 24 pixels for a total swath of 1920 km, 142 providing global coverage in 1.5 day. Each pixel has a size of 80x40km². After the launch of Metop-B, the GOME-143 2A swath was reduced to 960 km in July 2013, leading to ground pixel two times smaller.

144 **3. Description of the Algorithm**

145 The algorithm for retrieving tropospheric vertical columns of glyoxal relies on a classical DOAS approach (Platt 146 and Stutz, 2008). This approach consists first in fitting measured optical depths in an optimized spectral window 147 to derive the so-called slant column densities SCDs (atmospheric concentration integrated along the effective light 148 path) of the absorbers. The latter are thereafter converted into vertical column densities VCDs (concentration 149 vertically integrated from the satellite ground pixel up to the top of the atmosphere) with air mass factors (AMFs) 150 obtained by modelling the radiative transfer through the atmosphere. An additional background correction 151 procedure is often applied for weak absorbers such as glyoxal in order to reduce as much as possible the presence 152 of systematic biases caused by spectral interferences.

The glyoxal algorithm presented here largely inherits from past developments for predecessor nadir-viewing
satellite sensors (Alvarado et al., 2014, 2020; Chan Miller et al., 2014; Lerot et al., 2010; Vrekoussis et al., 2009;
Wittrock et al., 2006). Figure 1Figure 1 illustrates for one day of TROPOMI data the resulting main output of

156 every algorithmic components, which we further describe in the following sections, with emphasis on their

157 specificities. The retrievals are provided with estimates for the random and systematic errors, which are discussed

in subsection 3.4.



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Figure 1: Illustration of the different glyoxal algorithmic steps for one day of TROPOMI data (01/04/2020).
 (a) Glyoxal SCDs retrieved from the DOAS spectral fits; (b) Glyoxal AMFs; (c) Glyoxal normalized-SCDs resulting from the background correction procedure; (d) Final retrieved glyoxal VCDs. The data has been gridded at the spatial resolution of 0.25°.

164 **3.1. DOAS fit**

To exploit the glyoxal absorption bands, we use a fitting window from 435 to 460 nm encompassing the two most intense bands, which has shown in the past to provide reliable results (Barkley et al., 2017; Lerot et al., 2010). This has been confirmed by sensitivity tests carried out by Alvarado et al. (2014) and Chan Miller et al. (2014). Owing to its low optical depth ($<5x10^{-4}$), any poorly fitted feature in the radiance measurements may affect the retrieved glyoxal SCD. It is therefore crucial to account for any physical or instrumental effect in order to optimise the fit quality as much as possible. Different aspects of the algorithm contribute to achieve this. The wavelength grids of the measured spectra are recalibrated before the actual DOAS fits with a cross-correlation

procedure (Danckaert et al., 2017; De Smedt et al., 2018) during which the position of the lines in the measured irradiance spectrum is fitted to an external solar atlas (Chance and Kurucz, 2010), convolved to the satellite spectral resolution. This recalibration procedure is done once per orbit and separately for every detector row of the instrument.

176 Although the DOAS fit generally uses an irradiance as the reference spectrum, it is common practice, in the case

177 of weak tropospheric absorbers, to replace it by a mean radiance spectrum recorded in a remote region where the

- 178 concentration of the gas of interest is low (e.g. De Smedt et al., 2018). This allows reducing the presence of
- 179 systematic biases caused by spectral interferences and/or instrumental limitations. In particular, the use of one
- 180 separate mean radiance spectrum per detector row minimizes the presence of so-called stripes in the product

- 181 typical of imager-type instruments such as OMI or TROPOMI. Here we compute those mean radiance spectra on
- 182 a daily basis by averaging for each row all spectra located within the equatorial Pacific Ocean $(15^{\circ}S-15^{\circ}N)$;
- 183 120°W-180°W).
- 184 The selected settings for the DOAS fits rely on the aforementioned past studies and are summarized in Table 185 1Table 1. The latest available cross-sections for species absorbing in the selected fitting window are included in 186 the fit, i.e. O₃, NO₂, O₂-O₂, water vapour and liquid water in addition to glyoxal. Note that the water vapour cross-187 section has been generated for a temperature of 293K and a pressure of 1013hPa using the HITRAN2012 database 188 (Rothman et al., 2013) as we found that the latest HITRAN2016 version (Gordon et al., 2017) led to poorer fit 189 quality. Sensitivity tests have shown that the retrieved glyoxal SCDs are significantly impacted by the choice of 190 the H₂O cross-section but also of its temperature. Effective water vapour temperatures (computed as the mean of 191 temperature profiles weighted by typical H₂O concentration profiles) are generally close to our selected value in 192 regions with high water vapour content. This high sensitivity nevertheless points to the importance of having 193 accurate water vapour cross-section, especially in regards of its possible influence on glyoxal fields over oceans 194 (Chan Miller et al., 2014) (see section 4.2.3). The temperature dependence of the NO₂ absorption is taken into 195 account by including a second cross-section, taken as the difference between NO_2 cross-sections reported at 2 196 temperatures (220 and 294K) as proposed by Alvarado et al. (2014) and Chan Miller et al. (2014) for their 197 respective OMI glyoxal products. Consistently with Alvarado et al. (2014), we found that fitting the liquid water 198 optical depth in the glyoxal fitting window performs as well as fixing it to a value previously determined in a 199 larger spectral interval as proposed in the past (Lerot et al., 2010) with a limited presence of systematically 200 negative glyoxal columns over remote oceans. Vibrational Raman scattering on remote ocean water also 201 introduces some spectral structures caused by the filling-in of Fraunhofer lines. However, (Peters et al., 2014) 202 have shown the simultaneous fit of the liquid water cross-section and of an intensity offset (see below) efficiently 203 considers all remote ocean-related structures. A number of additional cross-sections are included in the fit to 204 consider (1) Inelastic scattering (Ring effect) introduces high-frequency structures that are treated as a pseudo-205 absorber (Chance and Spurr, 1997); (2) Intensity offsets in the spectra, caused for example by residual straylight, 206 are corrected for by fitting the inverse of the reference spectrum (Danckaert et al., 2017); (3) heterogeneity of the 207 scene brightness may also introduce high frequency structures, which are considered with pseudo-cross-sections 208 (more details hereafter). All those cross-sections are generated at the instrumental spectral resolution by using the 209 key data Instrumental Spectral Response Functions provided for all individual detector rows. During the DOAS procedure, the earthshine radiance spectrum is further aligned with the reference, by allowing it to be shifted and 210 211 stretched in wavelength. In addition, the DOAS fit procedure includes a spike removal scheme as described in Richter et al. (2011) enabling to filter out from the fit individual corrupted radiance measurements, and hence to 212 reduce the noise in the product. 213
- 214

Table 1 : Absorption cross-sections and settings used for the retrieval of glyoxal slant columns

Fitting interval	435-460 nm			
Absorption cross-sections				
Glyoxal	Volkamer et al. (2005)			

Ozone	Serdyuchenko et al. (2014), 223K, I_0 effect-corrected (Aliwell et		
	al., 2002)		
NO ₂	Vandaele et al. (1998), 220K and 294K, I_0 effect-corrected		
O4 (O2-O2)	Thalman and Volkamer (2013), 293K		
H ₂ O (vapour)	Rothman et al. (2013), 293K		
H ₂ O (liquid)	Mason et al. (2016)		
Scene Heterogeneity	2 pseudo-absorbers (Richter, 2018) – Internally generated		
Ring effect	Pseudo-absorber (Chance and Spurr, 1997; Wagner et al.,		
	2009)		
Other parameters			
Polynomial	3rd order		
Intensity offset correction	1 st -order offset (additional cross-section taken as the inverse of		
	the reference spectrum)		
Earthshine wavelength shift	1 st -order shift		
Reference spectrum (E ₀)	Daily average of radiances, per detector row, selected in		
	equatorial Pacific (Lat: [-15° 15°], Long: [180°-240°])		

216 **3.1.1. Scene heterogeneity**

Any intensity variation within the probed scene taking place perpendicularly to the instrumental slit (i.e. along 217 218 track) leads to perturbations of the instrumental spectral slit function (ISRF) (Noël et al., 2012; Voors et al., 2006). 219 Richter et al. (2018) have shown that those perturbations lead to a degradation of the NO₂ DOAS spectral fit 220 quality and to systematic biases on the retrieved slant columns. Such abrupt intensity changes occur for example 221 along the coasts, mountains or cloud edges. Glyoxal retrievals are also affected by such scene heterogeneity as 222 illustrated in Figure 2 Figure 2 over the Horn of Africa and Middle East. This figure shows in the panel (a) that 223 the root mean square (RMS) of the DOAS fit residuals is systematically higher along the coasts but also over land 224 where contamination by broken clouds or abrupt elevation changes cause discontinuities in brightness fields. The 225 stripes visible in this figure are due to the smaller pixel size (and hence lower signal-to-noise ratio) on the edges 226 of the across-track field of view. The panel (c) shows that there are some collocated artificial patterns 227 (positive/negative biases) in the mean retrieved glyoxal slant column field. The latter result from spectral 228 interferences with the signature introduced by the ISRF distortion. Richter et al. (2018) showed that those spectral 229 interferences can be significantly reduced with additional cross-sections in the DOAS fit scaling the possible scene 230 heterogeneity signature. Those cross-sections are generated with a statistical analysis of the fit residuals for many 231 observations in the Pacific Ocean as a function of the level of scene heterogeneity. The latter can be computed 232 using radiance measurements at higher spatial resolution available in the TROPOMI level-1 data at a limited 233 number of wavelengths. It ranges between -1 and +1 and is close to/deviates from 0 for 234 homogenous/heterogeneous scenes, the sign indicating the part of the ground pixel that dominates the scene 235 brightness. Following this approach, two additional cross-sections corresponding to the systematic residuals of 236 scenes with an heterogeneity factor larger/smaller than +/- 0.08 have been added to the DOAS baseline and both 237 the fit residuals and the identified glyoxal biases have been reduced as illustrated in the right panels (b) and (d) of

- Figure 2Figure 2. This effect is particularly visible along coasts and mountains but also over lands where some pseudo-noise caused by persistent broken clouds is also largely reduced. Although significantly correlated, including the two heterogeneity cross-sections leads to a further improvement of the fit quality, likely due to a slit
- 241 function perturbation that depends on the radiance distribution within the nominal ground pixel. Note that a third
- 242 cross-section derived from the mean residuals of homogeneous scenes is also added, which explains why the fit
- 243 RMS are also reduced (but less drastically) in homogeneous scenes. This cross-section has no impact on the
- 244 retrieved glyoxal SCDs and allowed mostly isolating systematic residuals due to scene heterogeneity only for the
- 245 pseudo cross-sections creation.



247	Figure 2 : Impact of scene brightness heterogeneity on glyoxal retrievals in the fitting window 435-460 nm over the
248	Horn of Africa and Middle-East. The panels (a) and (b) show mean fit residuals RMS for the year 2019 without and
249	with (left and right) pseudo-cross sections to correct for spectral signatures introduced by scene heterogeneity. The
250	panels (c) and (d) show the corresponding mean glyoxal slant column densities. Only observations with cloud
251	fractions less than 20% are considered.

252 **3.1.2.** Empirical correction for strong NO₂ absorption

The DOAS approach assumes that the wavelength dependence of the effective light path within the fit interval can be neglected. Although this assumption is generally reasonable, it may fail in case of strong absorption by one (or more) species, of which the slant column density becomes dependent on the wavelength (Puķīte et al., 2010). In that case, fitting the optical depth of that species by a simple scaling of its cross-section is inaccurate and the fit quality is degraded. Puķīte et al. (2010) have shown that fitting additional cross-sections resulting from a Taylor expansion of the wavelength-dependent slant column corrects for its variability within the fit window. As 259 mentioned before, the high sensitivity of glyoxal retrievals to potential sources of misfit was a motivation to 260 further investigate its sensitivity to extreme NO_2 concentration levels.

For this purpose, synthetic spectra were generated at a spectral resolution of 0.5 nm with the radiative transfer 261 262 model SCIATRAN (Rozanov et al., 2005) for a satellite nadir-viewing geometry and two different solar zenith 263 angles. In those simulations, inelastic scattering was neglected and a large range of tropospheric NO₂ columns 264 was covered by scaling the NO₂ a priori profile. The TROPOMI DOAS baseline described above was then applied 265 to those simulated spectra in order to retrieve CHOCHO SCDs and evaluate the error as a function of the NO₂ 266SCD as illustrated in Figure 3-Results clearly point to a CHOCHO SCD error increasing with the NO₂ SCD. Note that the exact error magnitude may change slightly depending on the NO₂ vertical distribution and on 267 the actual atmospheric content. On the other hand, adding two so-called Pukite cross-sections (Pukite et al., 2010) 268 269 resulting from a first order expansion of the NO₂ slant column around the wavelength and the vertical optical 270 depth significantly reduces the errors.



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Figure 3 : Absolute error (in molec/cm²) on the retrieved CHOCHO SCD as a function of the NO₂ SCD for simulated
 spectra in a nadir-viewing satellite geometry and for two solar zenith angles. The reference "true" CHOCHO SCD is
 taken as the value retrieved for the lowest NO2 SCD scenario. The error increases with the NO₂ SCD when Pukite
 cross-sections are not included in the fit, but remains small otherwise.

276 On this basis, the impact of adding the Pukite cross-sections to the DOAS baseline has been investigated using 277 one month of TROPOMI data. A wintertime period was chosen (December 2019) to favour the number of 278 observations with large NO₂ concentrations, in particular in China but also in other megacities in the Northern 279 Hemisphere. Figure 4 (upper panel) displays the monthly mean NO₂ SCDs in December 2019, and 280 (middle panel) the mean impact on the retrieved CHOCHO SCDs of introducing the Pukite terms in the DOAS 281 spectral fit baseline. The CHOCHO SCD differences caused by the Pukite terms are also plotted as a function of 282 the NO₂ SCDs to better visualize the correlation (lower panel). For regions with enhanced NO₂ concentrations 283 (>2x10¹⁶ molec/cm²) (e.g. China, India, Teheran), the Pukite cross-sections lead to a systematic reduction of the 284 CHOCHO SCDs, consistent with the closed-loop tests described above. A small improvement of the fit quality is 285 found (not shown). Unexpectedly, the impact of those additional cross-sections on the CHOCHO SCDs can also 286 be non-negligible in regions with low NO₂ columns: positive differences are for example observed over equatorial 287 oceans, but also over South America and Africa. The correlation plot of Figure 4-Figure 4 clearly shows these two 288 regimes. While the impact of the Pukite cross-sections on the glyoxal retrievals is understood and reliable for

289 large NO_2 SCDs, their influence at low NO_2 SCD is more questionable and likely results from spectral

interferences occurring between the different fitted spectra (e.g. with the Ring signature), which introduces

additional noise in the product.

- 292 To avoid this, rather than fitting additional cross-sections, we introduce an empirical correction applied to the
- 293 glyoxal SCDs. This correction consists in subtracting from the glyoxal SCD a NO₂-SCD dependent value, directly
- 294 prescribed from the linear regression fit through the sensitivity test results for all observations worldwide from
- 295 December 2019, with NO₂ SCDs larger than $2x10^{16}$ molec/cm² as illustrated in Figure 4 (c). It is worth
- noting that the regression fit results agree well with the glyoxal SCD errors estimated from the simulations
- 297 presented above (Figure 3Figure 3). For extreme pollution conditions such as what can be found in China during
- 298 Wintertime, this correction may lead to glyoxal column reduction up to 30%.



Monthly mean NO₂ SCD (molec.cm-2) - December 2019





CHOCHO SCD differences (molec.cm-2) - with-w/o Pukite

300Figure 4 : (a) Monthly mean NO2 SCDs retrieved from TROPOMI data in December 2019. Panel (b) illustrates the301CHOCHO SCD absolute differences (molec/cm²) due to the incorporation of the Pukite et al. (2010) cross-sections in

- 302 the DOAS spectral fit and panel (c) shows the correlation between those differences and the NO₂ SCDs. The red line
- 303 corresponds to a linear regression fit through all points with NO₂ SCD larger than 2x10¹⁶ molec/cm².

304 3.2. Air Mass Factor computation

The computation of the air mass factor (AMF) used to convert the retrieved glyoxal slant columns (SCD) to vertical columns (VCD) relies on the formulation of Palmer et al. (2001), which decouples the radiative transfer through the atmosphere from the vertical distribution of the gas of interest. Radiative transfer simulations are performed with the vector model VLIDORT at the middle of the fitting window (448 nm) to compute so-called altitude-dependent air mass factors or box-AMFs representing the sensitivity of the slant column to a small concentration change at any altitude. The AMF is obtained as the weighted mean of those box-AMFs using as weights the vertical distribution of the glyoxal concentration.

312 Typically, the sensitivity of nadir-viewing UV-Visible instruments is reduced in the lowermost atmospheric layers 313 because of Rayleigh scattering. However, this sensitivity depends strongly on the observation geometry, on the 314 surface reflectivity and altitude and on the presence of clouds. For example, the sensitivity is generally further 315 reduced for low sun elevation. For this reason, retrievals with solar zenith angles larger than 70° are filtered out. 316 We use a pre-computed five-dimensional look-up table of Box-AMFs spanning all observation conditions (see 317 Table 2Table 2) and from which appropriate values are linearly interpolated for every TROPOMI observation. 318 This interpolation uses as input the observation angles provided in the level-1 data, surface elevation taken from 319 the GMTED2010 topography (Danielson and Gesch, 2011) and surface albedo extracted from the OMI minimum Lambertian Equivalent Reflectivity climatology (Kleipool et al., 2008). The spatial resolution of the latter 320 321 database (0.5°x0.5°) is coarse compared to the TROPOMI footprint and neglects anisotropy, which may introduce 322 significant errors (Lorente et al., 2018). However, at the time of writing, it is the only database available at the 323 S5p overpass time although new Lambertian Equivalent Reflectivity climatologies relying on past works (e.g. 324 Loyola et al., 2020; Tilstra et al., 2021, 2017) are currently being prepared. On the other hand, the level of noise 325 in glyoxal retrievals generally requires averaging in space and/or time which in turn will reduce part of those error 326 sources. We also neglect the impact of clouds and aerosols on the radiative transfer. Instead we apply a stringent 327 cloud filtering approach: only observations with an effective cloud fraction (as retrieved in the same spectral range 328 and provided in the TROPOMI operational NO₂ product (van Geffen et al., 2019) lower than 20% are conserved. 329 This approach is motivated by the fact that glyoxal slant columns tend to be biased high over bright scenes because 330 of poorly understood residual spectral interferences (e.g. with the Ring signature). Similarly, scenes covered by snow and ice are also discarded. 331

- 332
- 333

Table 2 : Granularity of the Box-AMF look-up table

Parameter name	Grid of values			
Solar zenith angle [deg]	0, 10, 20, 30, 40, 45, 50, 55, 60, 65, 70, 72, 74, 76, 78, 80, 85			
Line of sight zenith angle [deg]	0, 10, 20, 30, 40, 50, 60, 65, 70, 75			

Relative azimuth angle [deg]	0, 45, 90, 135, 180
Surface albedo	0, 0.01, 0.025, 0.05, 0.075, 0.1, 0.15, 0.2, 0.25, 0.3 0.4, 0.6, 0.8, 1.0
Surface pressure [hPa]	1063.10, 1037.90, 1013.30, 989.28, 965.83, 920.58, 876.98, 834.99, 795.01, 701.21, 616.60, 540.48, 411.05, 308.00, 226.99, 165.79, 121.11

335 Typical monthly-dependent a priori glyoxal vertical profile shapes necessary to perform the AMF computations 336 have been calculated at the different satellite overpass times with the global Chemistry Transport Model 337 MAGRITTE developed at BIRA-IASB, which inherits from the IMAGES model (Bauwens et al., 2016; Müller and Brasseur, 1995; Stavrakou et al., 2009b, 2013). This model runs at 1°x1° resolution and calculates the 338 339 distribution of 182 chemical compounds, of which 141 species undergo transport. The modelled troposphere is 340 vertically divided in 40 levels between the surface and the lower stratosphere and meteorological fields are 341 provided by the ECMWF ERA-5 analyses. The chemical mechanism and deposition scheme have been recently 342 updated (Müller et al., 2018, 2019). Anthropogenic NMVOC emissions are provided by the EDGAR 4.3.2 343 inventory (Huang et al., 2017) for the year 2012. Biomass burning emissions are obtained from the Global Fire 344 Emission Database version 4 (GFED4s) (Van Der Werf et al., 2017). The emissions of isoprene and monoterpenes 345 are calculated using the MEGAN-MOHYCAN model (Guenther et al., 2012; Müller et al., 2008). The model also 346 incorporates biogenic emissions of methanol, methyl-butenol, ethylene, ethanol, acetaldehyde, formaldehyde and 347 acetone, as well as oceanic emissions of methanol, acetone, acetaldehyde and alkyl nitrates (Müller et al., 2019). 348 The global source of glyoxal in the model amounts to 47 Tg/yr (in 2013), of which about 4 Tg/yr are due to direct biomass burning emissions, and 18, 6, 9 and 9 Tg/yr are due to the atmospheric degradation of isoprene, acetylene, 349 350 aromatics and monoterpenes, respectively (Müller et al., 2019).

To account for the difference in spatial resolution between the model and the observations, a priori profiles are
rescaled to the effective satellite pixel surface elevation using the formulation proposed by Zhou et al. (2009).
Enhanced glyoxal concentrations have been detected over oceans in several studies (Coburn et al., 2014; Lerot et

- al., 2010; Sinreich et al., 2010), but current models cannot reproduce this. For this reason, over oceans, we use an
- a priori glyoxal concentration profile measured with an air-borne MAX-DOAS instrument over the Pacific Ocean
- during the TORERO campaign (Volkamer et al., 2015).
- 357 **3.3. Background correction**

As already mentioned, systematic (row-dependent) biases in the retrieved SCDs often remain due to small residual interferences with spectral signatures from other absorbers or due to instrumental effects. In the particular case of pushbroom imaging instruments such as OMI/TROPOMI, across-track row-dependent biases (so-called stripes) often occur due to the imperfect calibration of the different CCD detector rows. To reduce those biases, a background correction using observations in a remote reference sector is generally applied as part of the retrieval algorithm (e.g. Alvarado et al., 2014; Chan Miller et al., 2014; Lerot et al., 2010; Richter and Burrows, 2002; De

Smedt et al., 2018). The principle of this background correction is to add offset values to the retrieved SCDs to 364 ensure that the resulting mean VCD in a clean remote region match an a priori known tropospheric glyoxal 365 column. Here we use the Pacific Ocean as reference sector with a constant reference VCD of 1×10^{14} molec/cm². 366 367 This value was chosen according to independent measurements performed in this region (Sinreich et al., 2010) 368 since current global models fail to reproduce remote sensing glyoxal levels observed over oceans (Fu et al., 2008; 369 Myriokefalitakis et al., 2008; Stavrakou et al., 2009b). There is nevertheless an uncertainty related to this reference 370 value, which impacts the overall level of the product. This error component is further discussed in section 3.4.3 371 and is taken into account to estimate the total glyoxal VCD error. As all intermediate variables (SCD, corrected-372 SCD, AMF) are provided in the product, a user could recompute glyoxal VCDs using a different reference Pacific 373 value.

- 374 The background correction is applied on a daily basis in different steps:
- First, a destriping procedure such as proposed in Boersma et al. (2007) is applied consisting in an offset
 correction determined separately for each instrumental row, and relying on clear sky observations from
 the Equatorial Pacific Ocean (15°S-15°N, 165°E-220°E). The offset corrections are added to all glyoxal
 SCDs worldwide, considering their respective row.
- 379 2. Additionally to the high frequency stripes, a broadband row-dependent structure, of which the shape also 380 depends on the latitude, was identified as illustrated in Figure 5, panel (a). This figure compares 381 the row-dependence of mean uncorrected VCDs in the Pacific Ocean at Equatorial and Northern mid-382 latitudes. The two curves are somehow anti-correlated, meaning that the destriping correction based on 383 equatorial latitudes only as applied in step 1 is not sufficient and even reinforces the mid-latitude structure. The second step of the background correction aims thus at reducing this broadband row-384 dependent structure at all latitudes while maintaining the mean latitudinal distribution of the measured 385 background glyoxal columns. For this, Pacific Ocean measurements (40°S-40°N, 165°E-220°E) are 386 387 binned per 20° in latitude and in groups of 15 rows in a 2-dimensional matrix. For this step, we use reference VCDs depending on the latitude and resulting from the averaging of the binned VCDs along 388 the row dimension. A corresponding 2-dimensional matrix of SCD offset corrections is then computed 389 390 in order, once applied to the binned VCDs, the corrected values match the reference VCDs. Interpolation through this correction matrix provides offsets to be applied to all SCDs retrieved worldwide. For satellite 391 392 pixels out of the latitude range, no extrapolation is performed but instead, the nearest neighbour 393 correction values are taken.
- Finally, the overall level of the product is adjusted with a single offset correction to ensure that the mean
 of all clear-sky VCDs within the full reference sector (40°S-40°N, 165°E-220°E) is equal to 1x10¹⁴
 molec/cm². Panel (b) of Figure 5Figure 5 shows how the identified row dependence in the VCDs at
 different latitudes has been reduced. The general level of the columns has also been adjusted.
- 398
- 399



Figure 5 : Row-dependence of the glyoxal vertical columns of S5p orbit #5877 (December, 1st 2018) averaged in an
equatorial latitude band and in a Northern mid-latitude band. (a) No background correction is applied; (b) a latitudedependent background correction is applied.

404 **3.4. Uncertainty estimates**

400

405 Glyoxal tropospheric column retrievals are affected by many sources of uncertainties in the different components of the algorithm. The low glyoxal optical depth makes its retrieval highly sensitive to measurement noise and to 406 407 spectral interferences with strong absorption signatures of other species or with instrumental features. Although 408 the measurement noise can be reduced by averaging column retrievals from individual observations, spectral 409 interferences generally lead to residual systematic errors (biases), which cannot be easily eliminated. The 410 background correction described above aims at reducing those biases, but it has its own limitations. For example, 411 the reference glyoxal tropospheric column within the reference sector is poorly known. In addition to spectral fit 412 errors, there are also significant errors associated to the air mass factor calculations, mostly originating from input 413 parameters uncertainties. For estimating the total glyoxal column error, we assume that the different error 414 components are uncorrelated and can be summed quadratically as in (Boersma et al., 2011; Lerot et al., 2010; De 415 Smedt et al., 2008, 2018). If the glyoxal vertical column N_v is expressed as

$$N_{v} = \frac{N_{s} - \overline{(N_{s,0} - N_{v,0,ref} \times M_{0})}}{M}$$
(1)

416 with N_s the retrieved slant column, M the AMF, $(N_{s,0} - N_{v,0,ref} \times M_0)$ the background correction term where $N_{s,0}$, 417 M_0 , $N_{v,0,ref}$ are the slant columns, AMF, and the reference vertical column within the reference sector, the total 418 glyoxal vertical column error can be written as

$$\sigma_{N_{v}}^{2} = \frac{1}{M^{2}} \left(\sigma_{N_{s}}^{2} + N_{v}^{2} \sigma_{M}^{2} + \sigma_{N_{s,0}}^{2} + N_{v,0,ref}^{2} \sigma_{M,0}^{2} + M_{0}^{2} \sigma_{N_{v,0,ref}}^{2} \right)$$
(2)

where σ_{N_s} , σ_M and $\sigma_{N_{\nu,0,ref}}$ are the errors on the slant column, the air mass factor and the reference value used in the background correction, respectively. In the following subsections, we discuss the different contributions to each of those terms. Errors can affect the retrievals randomly or systematically (biases). While the main random error is caused by the propagation of the instrumental photon detector shot noise on the measured radiances, the other error components are considered as being systematic. It has however to be noted that the latter assumption

- 424 may lead to conservative systematic error estimates and to an underestimation of the product scatter, depending 425 on the time and spatial resolution of interest. In particular, uncertainties associated to the input parameters needed 426 for the AMF calculation are directly related to the resolution of the used databases and may appear as random at 427 coarser resolution. This has been discussed by Vigouroux et al. (2020) who attributed part of the scatter in
- 428 formaldehyde vertical column TROPOMI/MAX-DOAS differences to a random component of the AMF errors.
- 429

3.4.1. Slant column uncertainties

430 As mentioned above, the radiance measurement noise directly propagates into the glyoxal slant column retrieval 431 and leads to large random errors $\sigma_{N_{s,rand}}$ (or precision) due to the low glyoxal optical depth. Those are easily estimated using the fit residuals RMS and the covariance matrix of the cross-sections included in the fit (Danckaert 432 433 et al., 2017). In the visible spectral range, the TROPOMI signal-to-noise ratio is about 1600 over dark scenes. This leads to a glyoxal VCD precision (i.e. $\sigma_{N_{s,rand}}$ /AMF) in the range of 6-10x10¹⁴ molec/cm² as illustrated in 434 435 Figure 6, panel (d). This range of values is consistent with the scatter observed in the retrieved glyoxal 436 SCDs in regions without any significant glyoxal source. Over bright scenes, for example covered by clouds or 437 snow, those errors significantly drop because of the increased signal-to-noise ratio. For individual observations, 438 random errors dominate and averaging is needed to extract meaningful glyoxal signals.

- 439 There are also systematic errors associated to the DOAS spectral fit that are mainly dominated by absorption 440 cross-section uncertainties, by interferences with other species (O_4 , liquid water, Ring ...), or by other effects such 441 as residual stray light. Those contributions are difficult to assess and can only be estimated from sensitivity tests (Lerot et al., 2010). In general, this error term can be as high as $2-3\times10^{14}$ molec/cm². However, the use of a 442 443 radiance as reference in the DOAS fit and the application of a background correction removes a large part of the 444 systematic error in the slant column fit (see section 3). As those corrections are not always sufficient to eliminate completely the SCD systematic errors due to local conditions (local pollution, residual clouds,...), we set $\sigma_{N_{s syst}}$ 445 446 to 1×10^{14} molec/cm².
- 447 **3.4.2. AMF uncertainties**

The errors on the air mass factor depend on the input parameter uncertainties and on the sensitivity of the air mass
factor to each of them. This contribution can be broken down into the squared sum (Boersma et al., 2011; Lerot
et al., 2010; De Smedt et al., 2018) as

$$\sigma_{M,syst}^2 = \left(\frac{\partial M}{\partial A_s} \cdot \sigma_{A_s}\right)^2 + \left(\frac{\partial M}{\partial s} \cdot \sigma_s\right)^2 + (0.15M)^2 \tag{3}$$

451 where σ_{A_s} and σ_s are typical uncertainties on the surface albedo and profile shape, respectively.

The contribution of each parameter to the total air mass factor error depends on the observation conditions.
Therefore, a small table of air mass factor derivatives spanning all observation conditions was computed using
VLIDORT, considering glyoxal box profile shapes with different effective heights.

455 The AMF error component related to the surface reflectivity (1st term of Eq. (3(3)) is calculated using an estimated 456 uncertainty on the albedo σ_{A_s} of 0.02 (Kleipool et al., 2008). Note that this uncertainty can be occasionally larger, 457 in particular at high latitudes where snow falls may cause abrupt changes in scene albedo. The uncertainty associated to the a priori profile shapes (the smoothing error) used in the retrieval is more difficult to assess, especially due to the scarcity of independent glyoxal profile measurements. For every observation, an effective height corresponding to the a priori glyoxal profile used in the AMF calculation is derived and used to extract the appropriate AMF derivative and σ_s is taken equal to 50hPa. The latter value corresponds to the typical standard deviation of the model profile shape effective heights over polluted regions.

Formulation (3(3)) is valid for clear sky pixels and the stringent cloud filtering we use. However, residual clouds undoubtedly impact the radiative transfer and generally shield the lowermost atmospheric layers. Therefore, we anticipate that the clear sky assumption generally leads to a low bias on the retrieved glyoxal columns in case of residual clouds. On the other hand, the spectral interferences over bright (cloudy) scenes as discussed in section 3.2 impact the retrievals the other way round. The third term in equation (3(3) accounts for possible errors in the AMF model itself, including the neglect of aerosols and clouds, wavelength dependence,..., and is estimated to be 15% of the air mass factor (Lorente et al., 2017).

470

3.4.3. Background correction uncertainties

471 Although the background correction is designed to overcome systematic features/deficiencies of the slant column 472 fitting, some errors are also associated to this procedure. In particular, systematic errors on the reference slant 473 columns and their air mass factors are propagated into the computed correction values. Also, there is an uncertainty 474 related to the reference glyoxal vertical column value in the reference sector as mentioned in section 3.3. The three last terms of Eq. (2(2) represent the total background correction uncertainty in which $\sigma_{N_{s,0}}$ is the systematic 475 slant column error fixed to 1×10^{14} molec/cm² (see above section 3.4.1), and M_0 and σ_{M_0} are the air mass factors 476 477 and their associated errors within the reference sector. In practice, those quantities are treated similarly as the reference slant columns (i.e. binned in latitude and row bins – see section 3.3). $\sigma_{N_{p,0,ref}}$ represents the error 478 associated to the reference value $N_{v,0,ref}$ and is fixed to 5×10^{13} molec/cm². Using a different reference value would 479 480 directly impact the overall level of glyoxal VCDs worldwide, with some small modulations related to the ratio of 481 the AMFs over Pacific and in other regions following Eq. (1(4)).

482

3.4.4. Total systematic uncertainties

Figure 6Figure 6, panel (c) shows the estimated mean VCD systematic errors for the month of June 2018 when all systematic error sources are combined together using Eq. (2)(2). Note that the conversion of the AMF error into an absolute vertical column error $(2^{nd}$ term of the equation) requires this error to be multiplied by the corresponding vertical column. Because of the high level of noise in the product, using the retrieved column for this would lead to a strong overestimation of the systematic error. To circumvent this, we use instead pre-computed climatological glyoxal noise-free VCDs.

489 Total glyoxal VCD systematic errors are generally in the range 1-3x10¹⁴ molec/cm², corresponding to about 30-

490 70% for emission regimes (columns larger than $2x10^{14}$ molec/cm²). Figure 7 shows the zonally averaged total

491 systematic error along with its different components for one S5p orbit passing over Africa. In general, the three

492 components contribute similarly to the total error for emission conditions. On contrary, the AMF error becomes

493 smaller in background conditions while the two other terms dominate. Note that pixels strongly contaminated by







Figure 6: (a) TROPOMI June 2018 monthly means of glyoxal tropospheric columns, glyoxal air mass factors (panel
(b)) and glyoxal tropospheric column systematic errors (panel (c)). Scenes contaminated by clouds or Ice/snow have
been filtered out. Panel (d) shows glyoxal tropospheric column random errors for one single day, in which all

509 observations have been kept to illustrate the impact of the scene brightness.



Figure 7 : 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.

513

4. Comparison with other satellite instruments

514 4.1. Algorithmic differences for GOME-2A/B and OMI glyoxal retrievals

515 Glyoxal tropospheric columns have also been retrieved from other satellite instruments, namely GOME-2 on 516 board the platforms Metop-A and –B and OMI on board AURA. Retrieval settings very similar to those described 517 in the previous section were applied. For GOME-2A and B, we use data records recently produced within the 518 operational environment of the EUMETSAT AC SAF (Valks et al., 2020). We list here the remaining differences 519 with respect to the TROPOMI algorithmic baseline and the specificities for each instrument.

520 All data sets essentially share the same DOAS fit settings (reference cross-sections, fit window, polynomial 521 degree...). The heterogeneity cross-sections are omitted for the GOME-2 and OMI retrievals. While the 522 instrumental design of GOME-2 makes it weakly sensitive to scene heterogeneity, it would be beneficial for OMI 523 to include similar cross-sections but that would imply a reprocessing of the complete slant column data set data 524 with limited added-value for the large-scale comparison with TROPOMI that we present in the next subsection. 525 For the GOME-2 instruments, we also fit two additional cross-sections representative of the instrumental 526 sensitivity to light polarization as provided from the level-1 key data (EUMETSAT, 2011) as well as one pseudo 527 cross-section to account for an along-track spectral resolution change occurring due to instrumental temperature 528 change (Azam and Richter, 2015). Note that for GOME-2 the cross-sections are convolved with an instrumental 529 slit function optimized as part of the wavelength calibration for every measured irradiance (De Smedt et al., 2015), 530 which allows accounting for the known long-term drift of the GOME-2 instrument spectral response function.

531 Differences in air mass factor calculations consist only in using, over land, a priori profiles provided by

532 IMAGESv2, the chemical transport model predecessor of MAGRITTE, at the coarser resolution of 2.0°x2.5°. For

533 the GOME-2 instruments, we use the directionally dependent Lambertian-equivalent reflectivity database

534 produced by Tilstra et al. (2021) instead of the OMI database.

535 A background correction procedure is applied consistently with the one used for TROPOMI. The GOME-2

- 536 instruments being whiskbroom scanners, there is no destriping procedure as such but instead a viewing zenith
- angle-dependent correction is applied, also relying on the slant columns retrieved in the Equatorial Pacific sector.
- 538 This correction may account for example for remaining biases related to the instrumental polarization sensitivity.
- 539 For both OMI and GOME-2, the row/VZA dependence does not show any obvious change along the orbit and the
- 540 corresponding correction thus relies only on the low latitude measurements.

Note that the OMI and GOME-2 glyoxal products are filtered for cloudy scenes using cloud fraction lower than 20% as taken from the O₂-O₂ (Veefkind et al., 2016) and OCRA (Lutz et al., 2016) cloud products, respectively. The empirical correction for strong NO₂ absorption signature described in section 3.1 has been applied to those instruments as well. In the following section, we compare the TROPOMI glyoxal retrievals with the OMI and GOME-2A/B data sets. The OMI record covers the period 2005-2018, while GOME-2A/B span the periods 2007-2017 and 2013-2020, respectively. OMI and GOME-2A records were interrupted when their respective quality was degraded too severely and other instruments were available to continue the morning and afternoon time series.

548

4.2. Glyoxal satellite inter-comparison

549 **4.2.1.** Comparison of the noise level

550 As mentioned before, the level of noise in the satellite glyoxal tropospheric column products is large compared to 551 the real signal. This is illustrated in the upper panel of Figure 8 Figure 8 which shows all individual clear-sky 552 TROPOMI glyoxal columns retrieved in the Pacific Ocean on June, 1st 2018 and plotted as a function of their latitude. The scatter is significant ($\sigma \approx 5-7 \times 10^{14}$ molec/cm²) with respect to the small glyoxal VCDs averaged in 553 554 5° -latitude bins in this sector. The lower panel compares the standard deviation of the retrievals from TROPOMI, 555 OMI, GOME-2A and B in the same remote sector for the 1st of June of their respective first year of operation. The 556 scatter in the retrievals is directly linked to the instrumental signal-to-noise ratio, which is documented to be 557 around 500 for OMI (Schenkeveld et al., 2017), 1000 for GOME-2 (Zara et al., 2018) and 1500 for TROPOMI (Kleipool et al., 2018). In practice, we see that the CHOCHO observation noise is indeed slightly larger for OMI, 558 559 that GOME-2B retrievals are noisier than those from GOME-2A, which have a level of noise similar to 560 TROPOMI. Considering the very small footprint size of TROPOMI (3x7.5 km² and 3x5.5 km² after August 2019) compared to the other instruments (GOME-2: 80x40 km²; OMI: 13x24 km² at nadir), the TROPOMI observation 561 562 noise is remarkably low. More importantly, the much larger amount of TROPOMI data compared to OMI (~15x) 563 and GOME-2 (~100x) allows maintaining a better time or spatial resolution for a given target noise level. For example, the random error associated to the daily glyoxal column averaged in an area defined by a circle with a 564 radius of 50 km will be less than 0.5x10¹⁴ molec.cm⁻² for TROPOMI, while it will remain larger than 2.5x10¹⁴ 565 566 molec/cm² and 4.0x10¹⁴ molec/cm² for OMI and GOME-2, respectively.

This is illustrated in Figure 9Figure 9, which compares January monthly mean glyoxal VCD fields over Asia at the resolution of 0.05° for TROPOMI and OMI (upper panels) and 0.25° for GOME-2A and OMI (lower panels) after one year of their respective operation. At the resolution of 0.05°, the level of noise in the TROPOMI glyoxal map is very low and many details can be distinguished in the glyoxal spatial distribution. In particular, hot spots of glyoxal over many megacities are clearly identified (e.g. over Bangkok, New Delhi, Ho Chi Minh City,

- 572 Shenzhen...) but also over Cambodia where large fires occur every year from January to March. At this resolution
- 573 of 0.05°, the level of noise in the OMI map remains high and prevents distinguishing such details. At the coarser
- 574 spatial resolution of 0.25°, the reduction of the noise in the OMI and GOME-2 monthly glyoxal fields appears to
- be sufficient to better distinguish the glyoxal spatial distribution but at the cost of a significant smoothing. In the
- 576 next section, we will intercompare the four satellite products at low temporal and spatial resolution in order to
- 577 minimize the impact of the noise and to identify possible systematic discrepancies.





579 Figure 8 : Illustration of the level of noise in satellite CHOCHO VCD retrievals. The upper panel shows all clear sky 580 individual glyoxal VCDs retrieved in the Pacific Ocean from TROPOMI observations on June, 1st 2018. The scatter is 581 very large compared to the low real signal as illustrated by the data binned in 5° latitude bands. The lower panel 582 compares the standard deviation of the retrievals in the same sector from TROPOMI, OMI, and GOME2A/B on the 583 1st of June of their respective first year of operation.





586 Figure 9: Illustration of the impact of the instrumental signal-to-noise and available amount of data on monthly mean 587 glyoxal VCD fields retrieved from different satellite instruments. The (a) TROPOMI data for January 2019 gridded

588 at a resolution of 0.05°, (b) OMI data for January 2006 gridded at a resolution of 0.05°, (c) GOME-2A data for

589 January 2008 gridded at a resolution of 0.25°, and (d) OMI data for January 2006 gridded at a resolution of 0.25°.

590 Cloudy scenes have been filtered out and a smoothing filter has been applied on the four presented fields based on a

591 spatial mean with the nearest neighbouring grid cells.

592

4.2.2. Comparison of mean glyoxal fields

593 First, Figure 10Figure 10 and Figure 11Figure 11 compare seasonal maps of glyoxal VCDs generated from 594 TROPOMI, OMI and GOME-2A/B data products. In order to reduce the data scatter for each instrument, those 595 maps are based on long time series as indicated in the figures. Therefore, a one-to-one match is not expected. As 596 can be seen, the consistency between the four instruments is excellent. Glyoxal patterns are captured similarly for 597 all seasons in terms of both spatial distribution and VCD values. The largest glyoxal columns are observed in 598 tropical regions, where biogenic emissions are important, and in regions with important fire events (e.g. Amazonia 599 and Northern Africa in SON, Thailand/Indochina in MAM, Western US in August,...). At mid-latitudes, the glyoxal columns follow the seasonal cycle of biogenic activity with maximum values during summertime. 600 601 Localized hot spots of glyoxal are visible over megacities corresponding to strong anthropogenic emissions (e.g. Northern China Plain, Bangkok, Teheran, New Delhi, Sao Paulo...). 602

In contrast to TROPOMI and OMI, the level of noise in the GOME-2 data sets significantly increases over the South Atlantic Anomaly despite the application of a spike-removal procedure (section 3.1). Overall the GOME-2B maps are noisier than those from other sensors due to the lower signal-to-noise ratio of the spectra and a shorter time series. Compared to the UV, the sensitivity to the surface is larger in the visible, which may introduce

607 interferences with the spectral signature of specific ground surfaces, and thus may potentially lead to a bias on the

retrieved columns. A striking example is over the Kara-Bogaz-Gol near the Caspian sea, which is one of the

- saltiest lakes in the world and contains large concentrations of sediments (Kosarev et al., 2009). The glyoxal signal
 detected over that lagoon is unlikely to be physical and likely originates from interferences with the ground
- 611 reflectance spectral signature.



- 613 Figure 10: Comparison of long-term averaged global CHOCHO VCDs (in 10¹⁴ molec/cm²) derived from
- 614 GOME-2A, GOME-2B, OMI and TROPOMI sensors, for the March-April-May period (left panels) and
- 615 the June-July-August period (right panels).



Figure 11: Comparison of long-term averaged global CHOCHO VCDs (in 10¹⁴ molec/cm²) derived from
 GOME-2A, GOME-2B, OMI and TROPOMI sensors, for the September-October-November period (left
 panels) and the December-January-February period (right panels).

For a more detailed investigation of the consistency of the TROPOMI data set with OMI and GOME-2A/B, we
 compare complete time-series of monthly median glyoxal columns in selected regions (shown in Figure

622 12Figure 12). The red rectangles indicate the regions on which we focus in Figure 13Figure 13 and Figure

- 623 14Figure 14, while the global statistics for all highlighted regions are given in Figure 15Figure 15. Detailed
- 624 figures are provided for all regions as supplementary material (Figures S1, S2, S3, S4). Figure 13Figure 13
- 625 compares directly the four full time series, while Figure 14Figure 14 compares the typical climatological
- 626 seasonal variations as obtained by combining all available years. The error bars in the latter figure represent the
- 627 interannual variability, and the 2-sigma standard deviation of the four satellite products is indicated as inset.
- 628 In the Tropics (e.g. Amazonia, Equatorial/North Central Africa), the four data sets are relatively stable over time.
- 629 All instruments observe similar seasonal cycles and column values, although OMI appears to be slightly lower

- than the others, in particular in Equatorial Africa. The inter-annual variability in Amazonia is high compared to
- other regions worldwide. Glyoxal is produced in that region to a large extent by fire emissions, which are highly
- variable. There is a direct correlation between years with high glyoxal columns and large fire emissions (e.g. 2007,

633 2010, 2015, 2019) as derived from the GFED database (van Der Werf et al., 2017;

634 <u>https://www.globalfiredata.org/</u>).Interestingly, glyoxal columns measured by the morning GOME-2 instruments

are larger than the OMI columns in the early afternoon during the fire seasons. This is consistent with the diurnal

variation measured in satellite HCHO columns by De Smedt et al. (2015) and would deserve further investigation.

- 637 Other regions display a more regular seasonal cycle, consistently seen by the four instruments.
- 638 In Asia, there are many hot spots, of which the origin is manifolds and strongly depends on the region and season. 639 In addition to biogenic activities, large emissions due to fires may significantly contribute to the glyoxal columns. 640 As illustrated in Figure 14Figure 14, in the Indo-Gangetic Plain, there are typically two fire seasons in April/May 641 and in October/November (after the Monsoon period) related to agricultural burning of wheat residue (Kumar et 642 al., 2016), and leading to two maxima in the glyoxal VCD seasonal cycle with a significant interannual variability. For example, during the COVID-19 Indian lockdown in April/May 2020, fire activity has been reduced leading 643 to smaller emissions (Levelt et al., 2021). This region is also highly populated, causing large emissions due to 644 645 human activities. This is also true in North-East China where glyoxal columns remain significant in winter, while 646 biogenic emissions are low during that period of the year. Although less variable than fire emissions, 647 anthropogenic emissions may also change over time. Despite those variable emissions, the four data sets spanning different time periods show a high level of consistency. In China, it seems that the glyoxal columns as observed 648 649 by OMI, GOME-2A and B are slightly reduced after 2014. This would deserve further investigation. On the other 650 hand, any interpretation based on long-series of OMI data must be treated carefully since the instrument suffers 651 from an evolving row anomaly (Schenkeveld et al., 2017), which impacts the stability of the product and causes 652 an increasing number of outliers, especially at mid-latitudes. For example, over the Indo-Gangetic Plain, the OMI 653 columns deviate regularly from the other instruments after 2014. In general, remnants of noise are also visible in 654 the GOME-2 time series, which show somewhat less smooth time series than TROPOMI.

At mid-latitudes, the lower sun elevation, especially during local wintertime, makes the retrievals more challenging. Nevertheless, a small maximum is consistently observed during the local summertime. During wintertime, TROPOMI columns appear slightly lower than those from the other satellites. As mentioned before,

658 the stronger impact of the row anomaly at mid/high-latitudes leads to a larger number of outliers in the OMI data

659 set and to a low bias in winter after 2013/2014.



- Figure 12 : TROPOMI glyoxal VCD distribution (in 1e14 molec/cm²) averaged on the period January 2018-December
 2020. The rectangles represent the regions where the glyoxal products from different satellites are intercompared with
 a specific focus on red regions in Figure 13Figure 13 and Figure 14Figure 14.



Figure 13: Comparison of the monthly median glyoxal VCD time series from GOME-2A/B, OMI and TROPOMI in a
 few selected regions worldwide.



Figure 14: Comparison of the climatological seasonal variation of the monthly median glyoxal VCDs from GOME2A/B, OMI and TROPOMI in a few selected regions worldwide. The error bars represent the interannual variability
as derived from the full time series.

674 Figure 15Figure 15 summarizes for all regions drawn in Figure 12Figure 12 the absolute and relative deviation of 675 each of the four data sets with respect to the median values of the ensemble. The symbols represent the median deviation considering all months of the year, while the error bars represent the full range of the monthly deviations. 676 Regions are sorted by increasing mean glyoxal vertical column amounts and light and dark blue shaded areas 677 indicate 2.5x10¹⁴ molec/cm² (50%) and 1.5x10¹⁴ molec/cm² (30%) differences as guidelines. Inter-satellite 678 deviations are generally less than 5×10^{13} molec/cm² (20%). The large error bars in the relative differences plot for 679 680 mid-latitude regions are caused by local wintertime months during which the glyoxal content is very low, if not negligible, and are therefore meaningless. Overall, the inter-satellite consistency of the glyoxal VCD products is 681

excellent. In the section 5, we will investigate the product quality with comparisons with independent ground based MAX-DOAS glyoxal observations at a few stations in Asia and Europe.



684

Figure 15: Median deviation of the glyoxal VCD differences for TROPOMI, OMI, GOME-2A/B against the median
value of the ensemble of the four data sets in the selected regions worldwide drawn in Figure 12Figure 12. Those are
plotted in absolute values (molec/cm²) in the upper panel and in relative values (%) in the lower panel. The error bars
indicate the full range of the deviations considering climatological monthly data. Regions are sorted by increasing
median glyoxal VCD value from left to right. The light and dark blue shaded area indicate differences of 1.5
molec/cm² (30%) and 2.5 molec/cm² (50%).

691 692

4.2.3. Glyoxal over equatorial oceans

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 696 697 past years, glyoxal measurements have been realized with ship-borne MAX-DOAS. While Sinreich et al. (2010) 698 measured glyoxal concentrations up to 100 ppt in the marine boundary layer of the Equatorial Pacific Ocean, most 699 other studies (Behrens et al., 2019b; Lawson et al., 2015; Mahajan et al., 2014; Volkamer et al., 2015) reported 700 lower concentrations inconsistent with the satellite elevated glyoxal columns. However, Volkamer et al. (2015) 701 also reported elevated glyoxal concentrations measured with an airborne MAX-DOAS in the free troposphere, 702 which might explain the larger satellite glyoxal signal. Remaining spectral interferences may also contribute, at 703 least partly, to this signal. In particular, its spatial correlation with high water vapour concentration regions and 704 the high sensitivity of glyoxal retrievals to the water vapour cross-section as discussed in section 3.1 and by Chan 705 Miller et al. (2014) call for a careful assessment of any future new data release or for future investigation on fit 706 strategy to mitigate this interference (e.g. Kluge et al., 2020).

707

708 5. Validation with MAX-DOAS data

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5.1. Description of MAX-DOAS data sets and methodology

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MAX-DOAS instruments measure scattered solar light in the UV-Visible spectral range at different elevation angles above the horizon and allow retrieving information on trace gases and aerosol extinction in the altitude range below 2-3km of the atmosphere, where the instrumental sensitivity is the highest. In a first approximation, vertical columns of boundary layer gases can be estimated from MAX-DOAS measurements using a simple geometrical approach (Brinksma et al., 2008; Hönninger et al., 2004). More elaborated approaches exploit a set of different elevation angles to derive information on the vertical distribution of the gas concentration with up to 4 degrees of freedom, resulting in more accurate vertical columns in the 0-4 km altitude range (e.g. Beirle et al.,

718 2019; Clémer et al., 2010; Irie et al., 2011; Friedrich et al., 2019).

719 Glyoxal concentrations can be derived from MAX-DOAS measurements in the visible range. However, the 720 number of glyoxal MAX-DOAS data sets is very limited, especially those covering a period long enough to allow 721 the validation of satellite data during entire seasonal cycles. Moreover, MAX-DOAS retrievals are affected by 722 similar difficulties as satellite retrievals (noise, spectral interferences). Here, we collected an ensemble of data 723 sets from nine stations located in Asia and Europe (see Table 3 Table 3) spanning at least one year. Altogether a 724 wide range of glyoxal columns and emission regimes are covered by those stations. Unfortunately, the approach 725 to retrieve glyoxal from MAX-DOAS has not been homogenized so far, and they cannot be considered as true 726 fiducial reference measurements. For example, although the same interfering species have been included in the 727 DOAS fits, the reference cross-section data as well as the fitting interval may vary. The design (spectral range, spectral resolution, detector type, etc.) and operation mode of the instruments differ substantially, resulting in 728 729 different sensitivities to changes in retrieval settings. Finally, the slant-to-vertical column conversion is performed 730 differently from one station to another (see Table 3Table 3). Despite those limitations, the comparison of glyoxal 731 tropospheric columns from satellites with nine different MAX-DOAS instruments is unprecedented. Among the available MAX-DOAS data sets, three (Xianghe/China, Chiba/Japan and Phimai/Thailand) are long 732

enough to allow a comparison with OMI and GOME-2A/B in addition to TROPOMI. The other ones span shorter,

has the longest and stable data record, and provide vertical profiles of glyoxal. Therefore we have used this reference station to perform a thorough analysis of the satellite product stability and of the impact of applying satellite averaging kernels. For the other stations, we performed a more qualitative comparison of the seasonal cycles of the glyoxal tropospheric columns. For the data colocation, we select MAX-DOAS data ± 1.5 hour around the satellite overpass time and satellite data within a radius of 100 km (150 km for Phimai) and 20 km around the station for GOME-2A/B/OMI and TROPOMI, respectively. Daily median glyoxal columns are computed if both satellite and ground-based data are available and finally monthly medians of the daily median columns are

and more recent periods and will be used only for comparison with the TROPOMI product. The Xianghe station

compared.

734

Table 3 : List of MAX-DOAS stations used in the study and brief description of the approach to generate the glyoxal
 data.

Station (coordinates) Time range	Institution PI	Retrieval Approach and fit interval	Reference	
Xianghe/China (39.75°, 116.96°E) 2010-2020 Uccle/Belgium (50.78°N, 4.35°E) 2017-2020	BIRA-IASB	Profile retrieved using an Optimal Estimation scheme 436-468 nm	(Clémer et al., 2010; Hendrick et al., 2014)	
Chiba/Japan (35.63°N, 140.10°E) 2012-2020 Phimai/Thailand (15.18°N, 140.10°E) 2014-2020 Pantnagar/India (29.03°N, 79.47°E) 2017-2020	CERES	Profile retrieved using a parametrization approach 436–457 nm	(Hoque et al., 2018; Irie et al., 2011)	
Mohali/India (30.67°N, 76.73°E) May 2019 - 2020	MPIC/IISERM	Profile retrieved using a parametrization approach 400-460 nm	(Beirle et al., 2019; Kumar et al., 2020)	
Athens/Greece (38.05°N, 23.80°E) 2018-2020 Vienna/Austria (48.18°N, 16.39°E) 2018-2020 Bremen/Germany (53.11°N, 8.86°E) 2018-2020	IUP-UB	Columns retrieved using the Geometrical Approximation 436-468 nm	(Alvarado et al., 2020b; Gratsea et al., 2016; Schreier et al., 2020)	

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747 **5.2. Validation results**

748

Figure 16Figure 16 focuses on the comparison of monthly median glyoxal tropospheric columns retrieved from TROPOMI, OMI, GOME-2A and GOME-2B with columns from the BIRA-IASB MAX-DOAS instrument in Xianghe (China). The left panels compare the full time series for each satellite sensor with the MAX-DOAS data record. The right panels show the corresponding satellite/MAX-DOAS absolute differences. Note that the MAX-DOAS measurements have been interrupted from mid-2018 to mid-2019 due to an instrumental problem. Overall,





- Figure 16 : Comparison of the monthly median glyoxal tropospheric vertical columns retrieved from satellite and
- 776 MAX-DOAS (MXD) instruments in Xianghe (China). The four left panels compare the time series from TROPOMI,
- 777 OMI and GOME-2A/B with the MXD time series. MXD columns are also shown when smoothed with the satellite
- averaging kernels. The error bars represent the 25 and 75% percentiles. The four right panels show the corresponding
- time series of the satellite-MD absolute differences. Both original and smoothed MXD data are shown. Mean bias and
- 780 standard deviation of the differences are given (in 10¹⁵ molec/cm² units) in the panel titles and are also represented in
- 781 the right panels with the full and dashed coloured lines.
- 782

In Figure 17Figure 17, we compare the median satellite and MAX-DOAS seasonal cycles of the glyoxal 783 784 tropospheric columns at three stations (Xianghe, Chiba and Phimai) where the time series present a good overlap 785 with the OMI and GOME-2A and B records, in addition to TROPOMI. In Xianghe, the seasonal cycle of the smoothed MAX-DOAS columns is also shown, illustrating again the reduction of the satellite/MAX-DOAS bias 786 when the a priori profile error component is removed. Note that the OMI and GOME-2B seasonal cycles are 787 788 computed using data until end of 2013 and 2016 to limit the impact of the increasing number of outliers. In each 789 comparison panel, the MAX-DOAS cycle is always computed using the same time range as the satellite 790 instrument. Overall, the seasonal patterns are consistently captured by the satellite and MAX-DOAS instruments. 791 In Xianghe, the GOME-2A and TROPOMI cycles follow closely the MAX-DOAS curves, although TROPOMI 792 slightly underestimates the MAX-DOAS columns during winter months. OMI and GOME-2B also reproduce the 793 general seasonal pattern but show a somewhat more scattered curve, likely due to their slightly less stable time series. In Chiba where the glyoxal signal is mostly driven by biogenic emissions, the agreement between the 794 795 satellites and the MAX-DOAS measurements is excellent both in terms of variability and absolute values. Again, OMI shows a larger scatter (as also indicated by the larger error bars representing the inter-annual variability). In 796 797 Phimai, where pyrogenic emissions are responsible for large glyoxal columns especially in the first few months 798 of the year, the seasonal variability seen by the satellites and the MAX-DOAS is very consistent. A negative bias 799 larger than for other stations is nevertheless observed. This can be related to other studies that identified larger 800 biases in NO₂ or HCHO DOAS products for elevated column conditions (e.g. De Smedt et al., 2021; Verhoelst et 801 al., 2021; Vigouroux et al., 2020). Possible causes for such biases are the different air masses probed by the 802 satellite and ground-based instruments, their different vertical sensitivity as well as the a priori vertical profile 803 information used in the retrieval algorithms.



Figure 17 : Comparison of the monthly median glyoxal tropospheric vertical column seasonal cycle as retrieved from
 TROPOMI, OMI, GOME-2A/B and MXD in Xianghe (China), Chiba (Japan) and Phimai (Thailand). The columns

correspond to the three stations and the rows to the different satellites. In Xianghe, MXD data smoothed with the
 satellite averaging kernels are also shown. The error bars represent the interannual variability (25% and 75%
 percentiles based on the full time series available). Note that the comparison of with the MAX-DOAS data in Phimai is

810 not shown as the latter starts in 2014 when OMI is degraded.

812 In Figure 18Figure 18Figure 18, we compare again the seasonal cycle of glyoxal VCDs retrieved from TROPOMI with that 813 from more recent MAX-DOAS time series at six different stations. Four of them are located at mid-latitude in 814 Europe and show relatively low glyoxal columns, while larger average values are measured at the two other 815 stations, in Northern India (Mohali and Pantnagar). In Vienna/Austria and Athens/Greece, TROPOMI and MAX-816 DOAS glyoxal columns agree very well and show consistent seasonal dependencies with maximum and minimum 817 values during summertime and wintertime, respectively. On the other hand, at the higher latitude stations of 818 Bremen/Germany and Uccle/Belgium, the consistency of the seasonal variations seen from space and from the 819 ground is somewhat poorer. While the glyoxal columns agree well during summertime, the satellite columns tend 820 to underestimate MAX-DOAS values in winter, the latter showing almost no seasonal variation. Satellite glyoxal 821 retrievals at those latitudes are challenging in winter because of the low sun elevation causing a reduced sensitivity 822 to the lowermost atmospheric layers. As mentioned in section 3.2, observations with solar zenith angles larger 823 than 70° are filtered for this reason, which explains the gap between November and January at those two stations. 824 In Uccle, we have also tested the impact of smoothing the MAX-DOAS columns with the satellite averaging 825 kernels (similarly as for Xianghe), which turned out to be very small. The absence of any seasonal dependence in 826 the cities of Brussels (Uccle) and Bremen, in contrast to that observed (although limited) in Vienna and Athens, 827 is to some extent puzzling. One should keep in mind however that the glyoxal retrievals from MAX-DOAS 828 measurements are also challenging and it cannot be excluded that errors in ground-based data might also partly 829 contribute to the observed differences.

830 In Mohali and Pantnagar, glyoxal columns are much larger and the seasonal variability is driven by fire emissions 831 and meteorological factors such as the monsoon. At those two stations, the glyoxal seasonal variability is very 832 well reproduced by TROPOMI. In terms of absolute values, the TROPOMI columns agree reasonably well in 833 Mohali but, they significantly underestimate the (large) MAX-DOAS columns in Pantnagar. The reason why the 834 systematic satellite/ground-based bias is so different between those two stations is unclear. MAX-DOAS columns 835 are clearly higher in Pantnagar than in Mohali pointing either to possible local differences in air quality, not 836 reflected in the satellite data, or to inconsistencies in the ground-based data sets. Although the agreement of the 837 absolute columns is reasonable in Mohali, the typical behaviour is an underestimation of the columns by the 838 satellites, as discussed before. Note also that those sites are significantly contaminated by aerosols, which are 839 neglected in the satellite retrievals (apart from the stringent cloud filtering). MAX-DOAS data have also been 840 analysed using very different approaches, which may also cause differences. This calls for a more detailed analysis, which would require an homogenization of the MAX-DOAS data treatment, a more sophisticated 841 842 approach for the computation of the satellite AMFs (e.g. with an explicit aerosol treatment) and possibly some 843 independent information on the glyoxal vertical distribution. This being said, the nice consistency in the glyoxal 844 column seasonal variability by the different systems is remarkable in itself. Table 4Table 4 provides an overview 845 of the correlation coefficient between the satellite and the MAX-DOAS glyoxal columns at all considered stations. 846 For stations where the analysis was possible for all satellite sensors, the correlation coefficient was found to be 847 significantly better for TROPOMI than for the other instruments. It is also clear that correlation coefficients are 848 better for sites characterised by large and highly variable glyoxal columns (e.g. Asian stations). Apart from the 849 Bremen station where the negative bias during winter leads to a low correlation coefficient, all other values are 850 quite reasonable (between 0.61 and 0.87) for TROPOMI. Table 4 Table 4 also gives the mean bias as derived from

- the comparison of the satellite and MAX-DOAS glyoxal column seasonal cycle as well as the standard deviation
- of the differences. As discussed above, the mean differences are generally lower than 1×10^{14} molec/cm², except for high columns where differences are noticeably higher.



Figure 18 : Comparison of the monthly median glyoxal tropospheric vertical column seasonal cycle as retrieved from
 TROPOMI and MXD at four European stations (Bremen, Uccle, Vienna, Athens) and at two Indian stations (Mohali,
 Pantnagar). The error bars represent the interannual variability (25% and 75% percentiles based on the full time

858 series available).

- 860 Table 4 : Correlation coefficients between the satellite and MAX-DOAS monthly median glyoxal tropospheric
- 861 vertical columns as well as mean absolute difference and associated standard deviation at nine stations.

	Correlation coefficient Mean bias \pm standard deviation (x10 ¹⁴ molec/cm ²)								
	Xianghe	Chiba	Phimai	Bremen	Uccle	Vienna	Athens	Mohali	Pantnag ar
TROPOMI	0.87 -0.8±0.6	0.80 <i>0.1±0.6</i>	0.85 -2.0±0.8	0.13 <i>-0.9±0.9</i>	0.67 -0.5±0.7	0.73 -0.3±0.6	0.61 <i>-0.4±0.6</i>	0.70 <i>0.6±0.9</i>	0.78 -3.5±1.5
OMI (until 2013)	0.70 -0.7±1.3	0.32 -0.6±0.8	N/A						

GOME-2B (until 2016)	0.37 -0.9±0.9	0.66 <i>0.0±0.</i> 7	0.88 -0.8±0.8			
GOME-2A	0.92 -0.8±0.4	0.58 -0.1±0.9	0.86 -1.1±0.8			

862 6. Conclusions

863 We presented the first global TROPOMI glyoxal tropospheric column product derived from three years (2018-2020) of visible radiance measurements. The DOAS-based algorithm, which relies largely on previous 864 865 developments for heritage satellite nadir-viewing instruments, has been further improved in different aspects. In particular, the use of additional pseudo cross-sections in the DOAS spectral fit allows mitigating the effect of the 866 867 instrumental spectral response function perturbations in case of scene brightness inhomogeneity, which otherwise 868 would lead to systematic biases in the retrieved glyoxal columns. This helps removing artefacts along the coasts 869 and reducing pseudo-noise in regions covered by persistent broken clouds. The glyoxal slant columns are also 870 empirically corrected for biases caused by the NO₂ misfit in case of strong absorption. Finally, the background correction procedure has been optimized for the TROPOMI characteristics and the a priori glyoxal vertical 871 872 distribution, essential to the AMF computation, is now provided by the CTM MAGRITTE, an updated version of 873 the IMAGES model, running at the higher spatial resolution of 1°x1°. The glyoxal column retrievals have been 874 fully characterized with an error budget considering the different error components introduced in each of the 875 algorithm modules. This allows extending the glyoxal column data product with total random and systematic error 876 estimates provided for every observation, with corresponding averaging kernels and a priori profiles.

877 Glyoxal tropospheric columns have also been derived from data of the OMI, GOME-2A and GOME-2B satellite 878 instruments using retrieval baselines similar to the TROPOMI algorithm. An extensive inter-comparison of those 879 four data sets emphasised their excellent consistency with absolute mean glyoxal column differences found to be generally lower than 0.5x10¹⁴ molec/cm². This demonstrates that glyoxal retrievals respond in the same manner 880 881 to our selection of settings for all nadir-viewing satellite instruments. Because of this sensitivity, the retrievals 882 may be easily impacted by spectral features caused by instrumental degradation. We have shown that the stability 883 of the OMI and GOME-2 data records is somewhat degraded after a few years of operations. Glyoxal retrievals 884 are characterized by a high level-of-noise, requiring significant spatio-temporal averaging to extract meaningful 885 signals. With both a much larger number of observations and a finer spatial resolution, TROPOMI outperforms 886 by far the previous instruments in its ability to provide high quality and detailed glyoxal fields. Although 887 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 888 889 measurements conducted in marine boundary layer campaigns. Non-negligible glyoxal concentrations in the free 890 troposphere as measured during one campaign (Volkamer et al., 2015) might reconcile the satellite and field data. 891 On the other hand, part of this signal may also be partly caused by remaining spectral interferences (e.g. with 892 water vapour).

Satellite observations have also been compared with a few independent MAX-DOAS data sets from stations
 located in Asia and Europe. Owing to the scarcity of MAX-DOAS glyoxal data sets, especially covering several

895 seasons, this validation exercise is therefore unprecedented. Based on a thorough analysis at the Xianghe station (China), where a 10-year time series of MAX-DOAS data is available, and on the comparison of seasonal cycles 896 897 at other stations, we conclude that satellite and MAX-DOAS instruments observe consistent glyoxal signals and 898 have similar intra-annual variations. This is reflected by the strong correlation coefficients, ranging between 0.61 899 and 0.87 for TROPOMI, with the exception of one mid-latitude station where the correlation is poorer. In general, 900 the satellite and MAX-DOAS columns also agree in absolute values with differences less than 1x10¹⁴ molec/cm², 901 at least for stations with moderate columns. In Xianghe, we showed that the application of the satellite averaging 902 kernels to the MAX-DOAS data further reduces the mean differences. There are however two stations 903 (Phimai/Thailand and Pantnagar/India) where the satellite/MAX-DOAS bias is more significant, despite a 904 reasonable agreement of the measured seasonal variations. Although the origin of this bias is not fully understood, 905 the MAX-DOAS columns at those stations are very high and it is not uncommon to have such biases in UV-906 Visible satellite retrievals for strongly polluted sites. It cannot be excluded that part of the bias originates from the 907 MAX-DOAS retrieval strategy at those sites. We have also indications that the satellite observations are low-908 biased during wintertime at mid-high latitudes where both the glyoxal signal is weak and the sensitivity to the 909 boundary layer is reduced. The comparisons of OMI, GOME-2 and MAX-DOAS glyoxal columns also show 910 reasonable agreement and similar intra-annual variability. Both the correlation coefficients and the scatter of the 911 satellite/ground differences were however less good than those of TROPOMI. This points again to the better 912 performance of TROPOMI for the detection of glyoxal from space and to its enhanced capability at providing 913 information on VOC emissions. For future work, it would be beneficial to dedicate more efforts in the 914 homogenization of the MAX-DOAS glyoxal retrievals in terms of both spectral analysis and slant-to-vertical 915 column conversion in order to strengthen their potential for the validation of satellite data sets such as the one 916 presented in this work.

917 Data availability

Access to TROPOMI glyoxal tropospheric column data is possible via the GLYRETRO website (https://glyretro.aeronomie.be/), OMI glyoxal data can be obtained on request from the authors. Information to download the GOME-2/Metop-A and GOME-2/Metop-B glyoxal data records is provided at https://acsaf.org/datarecord_access.php.

922 Author contributions

CL is the main contributor to the study and led the writing of this paper. FH performed the validation exercise,
with support from MVR and LMAA. MVR, LMAA, AR, IDS, NT, JV, HY and JVG contributed to algorithm
and/or code development. TS and JFM provides the a priori modelled glyoxal profiles. PV and DL are responsible
for the production of the GOME-2 glyoxal operational data records. MVR, FH, LMAA, SFS, HI, VK, TW, VS,
TiW and PW contributed to operating the MAX-DOAS instruments, and to producing and providing glyoxal data.
CR supervised the study. All co-authors have been involved into the discussion of results and the writing of this
article.

930 **Competing interests**

931 The authors have the following competing interests: Thomas Wagner is chief-executive editor of AMT. Andreas

932 Richter is executive editor of AMT. Diego Loyola, Andreas Richter, Michel Van Roozendael and Thomas

933 Wagner act as associate editors for AMT.

934

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- 947

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- 1393