

Total glyoxal column retrievals from GOME-2 backscattered light measurements

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Introduction

Glyoxal (CHOCHO) is the smallest dicarbonyl compound. Although mainly formed as an intermediate product in the oxidation of anthropogenic, pyrogenic and biogenic non-methane volatile organic compounds (NMVOCs), it is also directly emitted from fossil fuel and biofuel combustion and during fire events. Recent laboratory studies suggest that the uptake of glyoxal by clouds and aqueous aerosols leads to the formation of secondary organic aerosols (SOA) and could possibly account for part of the large SOA source missing from the current models.

Launched in October 2006 on board of METOP-A platform, the GOME-2 instrument measures the sunlight backscattered by the Earth's atmosphere between 240 nm and 790 nm. Compared to its predecessor ERS-2 GOME, GOME-2 is characterized by an improved spatial resolution (80 km x 40 km) and by a larger scan-width of 1920 km allowing for daily quasi-global coverage. Glyoxal presents structured absorption bands in the visible region between 400 nm and 460 nm, which can be used for total column retrieval with the Differential Optical Absorption Spectroscopy (DOAS) technique. The first global observations of glyoxal have been realized applying this technique to SCIAMACHY measurements by Wittrock et al.¹.

In this work, we present preliminary results of glyoxal slant and vertical columns from GOME-2. Based on the GOME-2 data of 2008, seasonal variations in the observed glyoxal columns are highlighted. These measurements are expected to provide better estimates of "top-down" glyoxal sources using inverse modelling techniques.

¹ Wittrock et al. (2006). Simultaneous global observations of glyoxal and formaldehyde from space, Geophys. Res. Lett., 33, L16804.

Differential Optical Absorption Spectroscopy (DOAS)

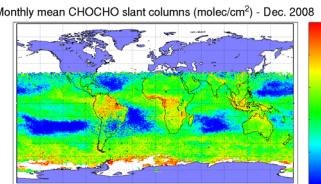
- The broad-band absorption features (from scattering, aerosols, ...) are filtered out by the adjustment of a polynomial of degree 2.
- The structured molecular absorption bands are used to retrieve the slant columns (concentration integrated along the light path) of different species.

DOAS retrieval settings

Reference	Daily sun irradiance spectrum. Shift adjusted in the DOAS retrieval.
Wavelength calibration	Cross-correlation on high-resolution Kurucz spectrum in the window (400 nm; 520 nm)
Absorption cross-sections	CHOCHO: Volkamer et al. (2005) at room temperature O ₃ : GOME FM98 at 243 nm (Burrows et al., 1999) NO ₂ : Vandaele et al. (1996) at 220K H ₂ O: HITRAN at room temperature O ₄ : Greenblatt et al. at 296K; wavelength axis corrected.
Ring (RRS)	Treated as a pseudo-absorber. Cross-section generated at GOME-2 resolution.
Intensity offset	Constant
Fitting interval	435 – 460 nm

Focus on oceanic regions

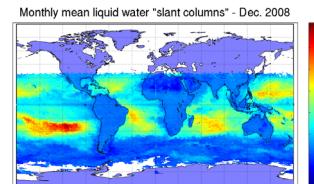
The figure on the right presents the mean glyoxal slant columns retrieved in December 2008:



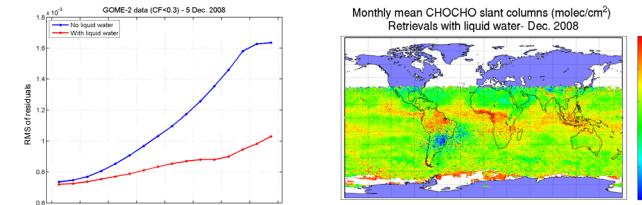
The persisting structures in the residuals over clear oceans partly originate from interference with the liquid water absorption spectrum. The quality of the glyoxal retrieval has been improved by considering the liquid water absorption in two steps:

1. Independent fit of an effective liquid water slant column:

DOAS retrieval settings	
Polynomial	5th order
Absorption cross-sections	Liquid water (Pope et al., 1997), O ₃ , O ₄
Fitting interval	405 – 490 nm



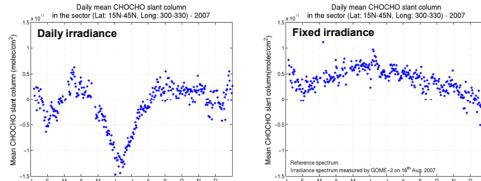
2. Glyoxal retrieval considering liquid water absorption parameterized by step 1:



Impact of the reference spectrum

Using the daily irradiance spectra measured by GOME-2 leads to yearly reproducible time-dependent offsets in the retrieved glyoxal slant columns possibly due to structures introduced by the diffuser plate of the instrument (Richter and Wagner, Technical note, 2001). As illustrated below, using a fixed solar spectrum leads to CHOCHO slant column variations much smaller.

→ Normalization of the slant columns by assuming a mean value of 2.8×10^{14} molec/cm² in the Atlantic reference sector (Latitude: 15°N–45°N, Longitude: 30°W–60°W).



Summary and conclusions

- DOAS settings have been established for retrieving glyoxal slant columns from GOME-2 backscattered light spectra.
- Above clear oceans, persisting structures in the residuals are reduced by considering the liquid water absorption; the retrieved CHOCHO columns are so physically meaningful. The quality of the fits could possibly be further improved by considering the vibrational Raman scattering due to liquid water and the phytoplankton absorption.
- Using the daily GOME-2 solar spectra as reference in the DOAS fits leads to time-dependent offsets in the retrieved slant columns. A normalization correction has been applied to minimize this artefact.
- The glyoxal slant columns are converted into total columns using air mass factors calculated with a radiative transfer model, and a-priori profiles from the CT model IMAGES v2.
- The GOME-2 total glyoxal data set from 2008 may be used to improve the estimates of glyoxal sources.

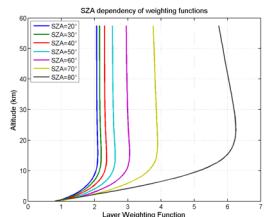
From slant columns to total columns

- The slant column is converted into a total column by means of the radiative transfer model DISORT, which is used for the air mass factor (AMF) calculation:

$$AMF = \frac{\int WF(h) \times \rho(h) dh}{\int h \rho(h) dh} \quad \begin{aligned} &\bullet \rho(h) \text{ is the glyoxal concentration (molec/cm³) at the altitude } h. \\ &\bullet WF(h) \text{ (weighting function) represents the GOME-2 sensitivity at the altitude } h. \end{aligned}$$

- Glyoxal profiles are provided by the CT model IMAGES v2 with a resolution of $4^\circ \times 5^\circ \times 1$ month (latitude x longitude x time).

- The weighting functions are calculated using DISORT at 448 nm. They depend on the geometry and the albedo and elevation of the reflecting surface.



Total glyoxal columns in 2008

- High total glyoxal columns are found above Africa, Asia (China, India, Indonesia) and South America where vegetation fires and biological activity are very intense.
- The anthropogenic emissions may also contribute to high glyoxal concentrations, especially in the Asia's megacities.
- Above Europe and North America, the glyoxal columns are moderate but significant, especially during warm season.
- The glyoxal measurements above equatorial oceans may imply oceanic emissions of the glyoxal precursors.
- Observed seasonalities in the glyoxal columns are related to temporal variations of the biogenic emissions and of the intensity of fires.

