

SATELLITE VALIDATION OF TROPOSPHERIC TRACE GASES WITH MAX-DOAS MEASUREMENTS DURING THE DANDELIONS FIELD CAMPAIGNS IN 2005 AND 2006

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ABSTRACT

This study presents time series for tropospheric amounts of formaldehyde (HCHO) and glyoxal (CHOCHO) retrieved from MAX-DOAS measurements at the DANDELIONS field campaigns that took place at Cabauw (The Netherlands) from May to July 2005 and in September 2006. These results are compared to SCIAMACHY satellite data. Both remote sensing techniques are in excellent agreement within their error bars. It is shown that the ground-based MAX-DOAS in combination with an automated profile retrieval is a powerful tool in establishing long-term observations of tropospheric trace gases and facilitating the validation of tropospheric column amounts from satellite instruments. The precision of the satellite data (monthly average) has been estimated to be about 4×10^{15} molec/cm² for HCHO and 2×10^{14} molec/cm² for CHOCHO.

1. INTRODUCTION

Methane (CH₄) and Non-Methane hydrocarbons (NMHC) are released into the atmosphere by a variety of natural and anthropogenic sources. The CH₄ oxidation ultimately produces HCHO, carbon monoxide (CO) and finally carbon dioxide (CO₂). NMHC react with hydroxyl (OH) radicals and other oxidizing agents, forming aldehydes, ketones and organic acids. In the presence of nitrogen oxides (NO_x), CH₄ and NMHC foster the photochemical production of ozone (O₃). HCHO is formed in most NMHC oxidation chains and also has known primary emissions from fossil fuel and biomass burning as well as industrial activities. They are, however, negligible compared to its large secondary source from volatile organic compounds (VOC) oxidation with the main single compound precursors methane and isoprene. HCHO is used as a proxy for VOC emissions. In spite of much progress in the last decade, emission estimates for the majority of NMHC remain quite uncertain (e.g. [1]).

Measurements of tropospheric HCHO have been made mainly on a campaign basis by both remote sensing and in situ techniques in urban and remote locations (e.g. [2] and references therein). With the launch of GOME (Global Ozone Monitoring Experiment) instrument in April 1995 formaldehyde measurements from space became feasible for the first time ([3] and references therein). Regions with elevated HCHO concentrations

have been identified using GOME observations and linked to biogenic isoprene emissions, biomass burning and also urban pollution (e.g. [4; 5]). However, only a few studies have compared and validated satellite data with ground-based and/or aircraft measurements [6; 7] Glyoxal, CHOCHO, the simplest alpha dicarbonyl organic compound, is similar to HCHO formed from the oxidation of a variety of hydrocarbons [8; 9]. Tropospheric CHOCHO has been measured during several campaigns. For example, in the boundary layer of a rural site, Lee et al. [10; 6] and Munger et al. [11] have reported mean mixing ratios of 0.07 ppb_v and 0.04 ppb_v glyoxal, respectively. The sources were thought to originate from isoprene rather than from anthropogenic emissions. Spaulding et al. [12] found lower values of about 0.03 ppb_v above a ponderosa pine plantation in California. [13] have identified CHOCHO and other aldehydes in air masses affected by biomass burning, domestic and residential log fires. In Volkamer et al. [14] glyoxal has been found in Mexico City as a secondary photochemical product in traffic related emissions with values up to 1.8 ppb_v, while direct CHOCHO emissions from traffic were small (<4%). This study also reported the first direct spectroscopic observations of CHOCHO in the atmosphere. During the day, photolysis and reaction with OH determine the CHOCHO lifetime. This was found to be 1.3 hours for overhead sun conditions, as compared to about 1.6 hours for HCHO [14]. Global observations of CHOCHO from space offer the potential of identifying photochemical hot spots in the earth's atmosphere [14], and coupled with observations of HCHO constrain our understanding of biogenic emissions, biomass burning, and urban pollution. Recently, the identification of glyoxal in measurements from SCIAMACHY has been reported [15; 16].

This study focuses on the validation of SCIAMACHY CHOCHO and HCHO columns by comparison with those derived from measurements by the Bremen ground-based MultiAxis DOAS instrument at Cabauw, The Netherlands.

2. INSTRUMENTS AND DATA RETRIEVAL

2.1. Satellite instrument SCIAMACHY

The SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric Cartography) is a spectrometer designed to measure sunlight, transmitted,

reflected and scattered by the Earth's atmosphere or surface in the ultraviolet, visible and near infrared wavelength region (240 nm – 2380 nm) at a moderate spectral resolution (0.2 nm – 1.5 nm) [8]. SCIAMACHY was launched on ENVISAT into a sun-synchronous orbit on 1st March 2002 having an equator crossing time of 10 AM local time (descending node). Global coverage is obtained within six days at the equator and within one day at 70° in spring. The spatial resolution varies between 30 km times 30 km and 240 km times 30 km depending on location and season. The ground pixel size used in this study is 30 km along track by 60 km across track.

Interpretation of the satellite measurements is complicated by the large diurnal variation of both trace gases, HCHO and CHOCHO, combined with the sun-synchronous orbit of the satellite. In order to facilitate systematic validation with the ground-based measurements, we here compare satellite-measured columns over the stations with the trace gas columns measured from the ground at the time of satellite-overpass.

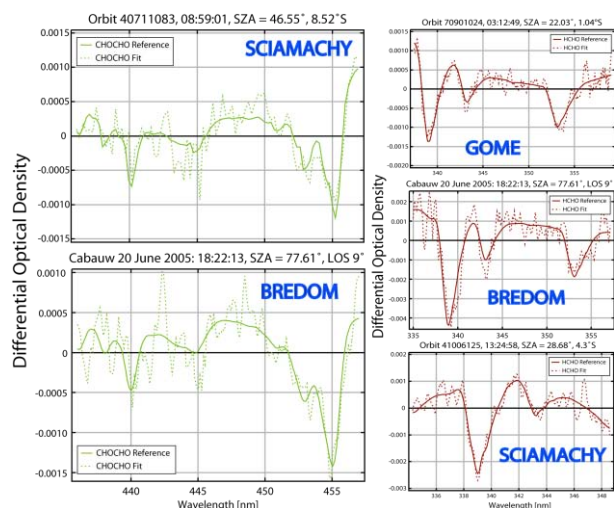


Figure 1. Fit examples for SCIAMACHY and the MAX-DOAS instrument (BREDOM). In addition, an example for a GOME HCHO fit residual is.

The obtained spectra are analysed with the well-known Differential Optical Absorption Spectroscopy (DOAS) method. The fitting procedure for HCHO includes, besides the HCHO cross section [17] and a fifth order polynomial for the compensation of broad-band features, the ozone (two temperatures), the nitrogen dioxide NO₂ (both [18]), the BrO [19] absorption cross sections as well as a rotational Raman scattering cross section [20]. Additional corrections have to be included to account for under-sampling and straylight of the instrument. The spectral region of the fit of 334 – 348 nm was selected to avoid any correlation with an instrument grating polarisation structure around 360 nm. For the determination of the CHOCHO column

amounts, the spectral region 436 – 457 nm was selected as optimal for fitting. In this case, the absorption cross sections of CHOCHO [21] O₃, NO₂, H₂O [22], O₄ [23], a Ring spectrum and a quadratic polynomial are included in the fitting procedure. For both trace gases a daily solar irradiance has been chosen as background for the DOAS retrieval.

The DOAS fit yields slant columns which have to be converted to vertical columns by an air mass factor, AMF. This accounts for the path of light through the atmosphere and takes the vertical profiles of scattering and absorbing species into account [24]. The AMF calculations for the satellite geometry use a priori knowledge of vertical trace gas profiles obtained from the ground-based observations (see below and [15] for details).

As an individual measurement of SCIAMACHY has only a very short exposure time and therefore limited signal to noise, all measurements within 100 km of the Cabauw station are averaged over a month. Only ground scenes having less than 20 percent cloud cover are considered. With these settings a typical precision of about 4×10^{15} molec/cm² for HCHO and 2×10^{14} molec/cm² for CHOCHO has been estimated for a monthly mean from satellite.

2.2. MAX-DOAS measurements at Cabauw

Two campaigns were held within the framework of the Dutch-nationally funded project DANDELIONS (Dutch Aerosol and Nitrogen Dioxide Experiments for vaLidation of OMI and SCIAMACHY). The primary goal was to validate OMI and SCIAMACHY nitrogen dioxide measurements, OMI and AATSR aerosol measurements, and OMI and SCIAMACHY column ozone measurements using groundbased and balloon observations, as well as models. A derived goal described in this paper was to assess the quality of SCIAMACHY formaldehyde and glyoxal measurements. The campaign location was the Cabauw Experimental Site for Atmospheric Research (CESAR, 51.971°N, 4.927°E). This site is located in the western part of the Netherlands in a polder 0.7 m below average sealevel. The nearby region is agricultural, and surface elevation changes are at most a few metres over 20 km, which makes it ideal for MAX-DOAS type measurements. The permanent instrumentation at this site is dedicated to all types of meteorological parameters. In 1972 a 213 m high mast was built for research on relations between the state of the atmospheric boundary layer, land surface conditions and the general weather situation.

Details about the MAX-DOAS instrument used in this study can be found elsewhere [24]. It was installed close to the ground about 300 m NE to the mast. Briefly, light is collected by a telescope with a moving mirror to enable near-simultaneous measurements of scattered light at multiple elevation angles (scans).

Similar DOAS retrieval settings as for the SCIAMACHY data are applied to the ground-based spectra. In contrast to the SCIAMACHY instrument for HCHO a somewhat larger fitting window of 337.5 to 357 nm has been chosen giving a lower detection limit. As back-ground spectrum, the zenith sky measurement from each scan is used. Fit examples for HCHO and CHOCHO are presented in Fig. 1.

The MAX-DOAS scans have been used to obtain both an accurate tropospheric column for the absorbing trace gas and profile information [24; 25; 15] applying a new algorithm: BREAM – **B**remian **A**dvanced **M**AX-DOAS Retrieval Algorithm.

In a first step the BREAM uses the radiation transport model SCIATRAN [26] to calculate O_4 slant columns which are compared to the measured ones in order to reduce uncertainties due to aerosols. The extinction profile in its total quantity as well as in its structure (i.e. the height of the boundary layer) is scaled in an iterative process and therewith the slant columns of O_4 are calculated. The quality of the agreement is evaluated by applying two parameters: The correlation between the measurement and the modelled columns (which is mainly influenced by the height of the boundary layer) and the mean deviation of those (mainly modulated by the extinction).

The second step comprises calculation of so called block air mass factors with respect to the chosen absorber using the prior obtained aerosol information. Again SCIATRAN in its full-spherical mode is operated. Block air mass factors are air mass factors which depend on the layer height of the absorber. The overall air mass factor is simply the average of the block air mass factors weighted by the distribution of the trace gas. This concept allows us to describe the relation between the measurement (i.e. the set of slant columns under different elevation angles of the absorber) and the absorber's profile in the atmosphere as a linear system:

$$y = K \cdot x \quad (1)$$

with y as the measurement vector, x the wanted profile and K as the weighting function matrix depending on the block air mass factors.

To solve such a linear system the well-known and in atmospheric chemistry long-established method of Optimal Estimation by Rodgers [27; 28] is appropriate. With this the profile x is determined by:

$$x = x_a + (K^T S_e^{-1} K + S_a^{-1})^{-1} K^T S_e^{-1} (y - K x_a)$$

y measurement (differential slant column)
 x_a a priori profile
 S_e and S_a error covariance matrices for a priori and measurement
 K weighting function matrix

$$K(i,j) = \frac{BDAMF(i,j) \cdot p(j) \cdot R \cdot N_A \cdot \Delta h}{T(j)}$$

$BDAMF$ block air mass factor relative to the reference
 p pressure, T temperature and Δh layer height

This method can only be applied for an optically thin atmosphere: The extinction of the light is mainly caused by scattering and consequently the radiative transfer independent from the concentration of the absorber. This constraint is valid for virtually all absorbers that can be retrieved via the DOAS method: NO_2 , all halogen oxides, formaldehyde and glyoxal, but fails for ozone in the ultraviolet spectral range or for line absorbers as H_2O .

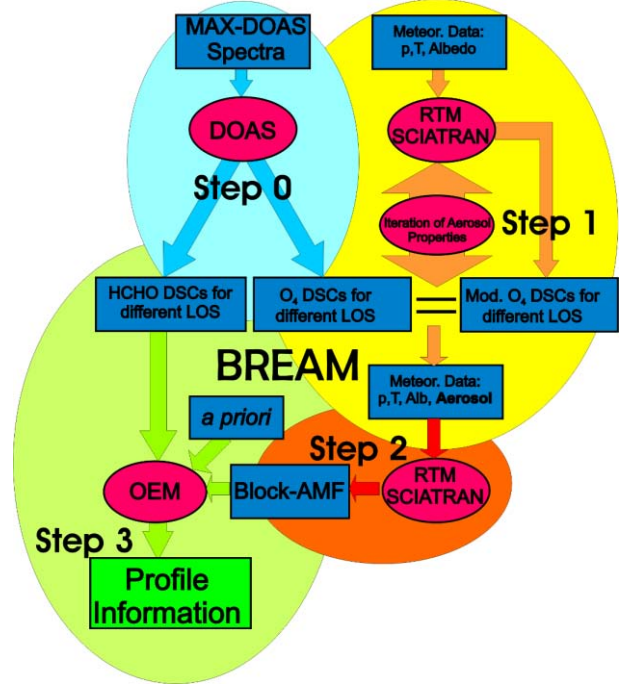


Figure 2. Flowchart of the different retrieval steps within BREAM (here illustrated for formaldehyde).

Exemplarily, Figure 3 is showing the profiles for HCHO and CHCHO retrieved from measurements in Cabauw on three consecutive days during the first DANDELIONS campaign. Glyoxal volume mixing ratios of up to 0.14 ppb_v and formaldehyde volume mixing ratios of up to 3.8 ppb_v are found. The maximum VMRs are present in the afternoon and close to the ground for both trace gases. The similarities for both species indicate that the sources of glyoxal and formaldehyde are quite alike.

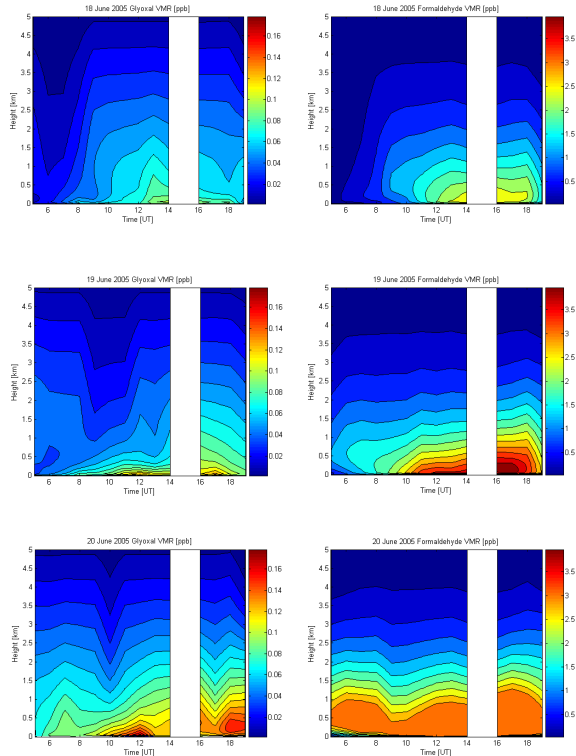


Figure 3. Profiles of CHOCHO and HCHO above Cabauw from 18 to 20 June 2005.

The profiles calculated by BREAM are used as input for the calculation of AMF for the satellite retrieval and to derive vertical columns shown in the next section. The quality of the retrieval algorithm has been illustrated in several case studies, e.g. by comparing to in-situ measurements from the ground (see [15] for details).

3. RESULTS

In Figures 4 and 5, the global composite of the CHOCHO and HCHO retrieved from SCIAMACHY are depicted using all data available from August 2002 to July 2006.

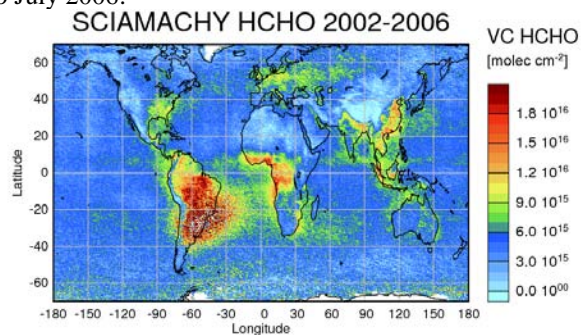


Figure 4. Composite of SCIAMACHY HCHO data.

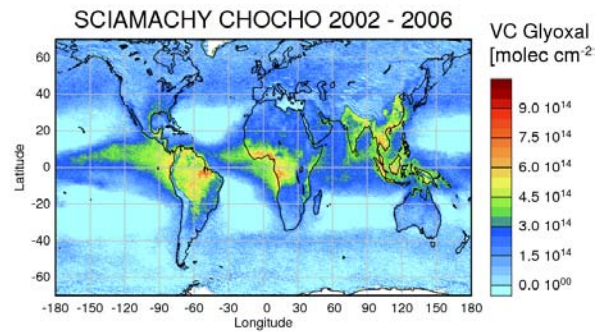


Figure 5. Composite of SCIAMACHY HCHO data.

Enhanced trace gas column amounts are mainly observed in South America, Africa and Asia. In South America, high column values can be found in the Amazon Basin, the world's largest tropical rain forest, and low values are found over the Andes. In Africa, enhanced CHOCHO and HCHO is found over the tropical rain forests and in regions having regular biomass burning events e.g. in Ghana. In Asia, large values are observed over Cambodia, Thailand, Sumatra, Borneo, south of the Himalaya mountains in India and Nepal and above densely populated areas in China. Generally, the pattern observed for CHOCHO is similar to the global picture of HCHO, indicating again common main sources.

CHOCHO column amounts retrieved over water are influenced by interference from liquid water absorption and potentially chlorophyll absorption leading e.g. to negative values above clear water bodies. Inclusion of liquid water and chlorophyll reference spectra in the fitting procedure for water ground scenes reduces the artefacts. Nevertheless, measurements over water have to be interpreted with care.

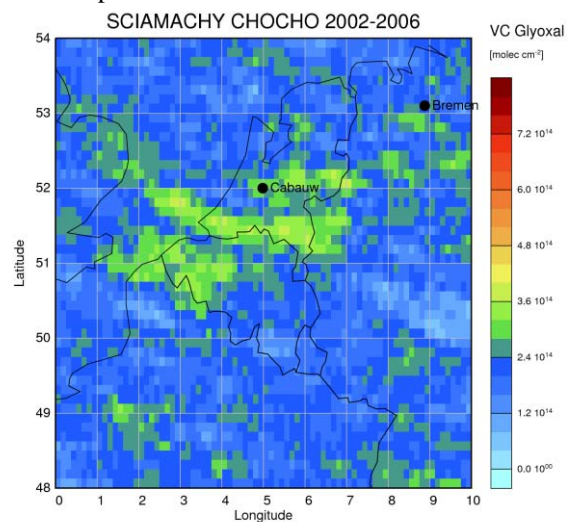


Figure 6. Composite of glyoxal data above Belgium and The Netherlands.

Figure 6 shows the composite of SCIAMACHY glyoxal data from 2002 to 2006 above the Benelux. It illustrates

the fact that this region is among the most polluted areas in Europe providing good opportunity to validate tropospheric trace gases.

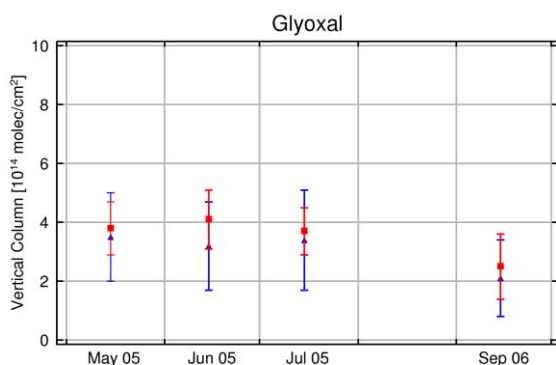


Figure 7. CHOCHO monthly means from MAX-DOAS (red) and SCIAMACHY (blue).

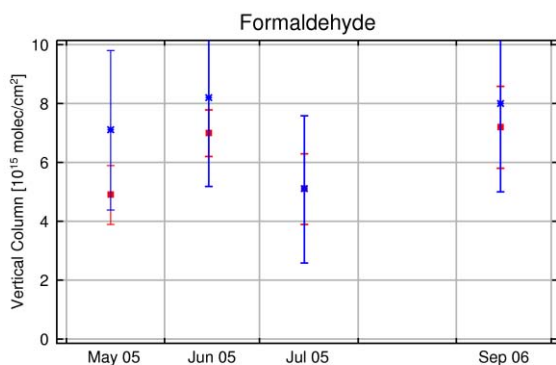


Figure 8. HCHO monthly means from MAX-DOAS (red) and SCIAMACHY (blue).

Figures 7 and 8 show the monthly means of the MAX-DOAS and the SCIAMACHY observations for glyoxal and formaldehyde. As already mentioned above, for the satellite only measurements with a cloud coverage less than 20 % and within a 100 km distance to the Cabauw site have been selected. The MAX-DOAS values are calculated using all data close to the SCIAMACHY overpasses (less than 2 hours). Overall a very good agreement has been found between both techniques well within the estimated error bars.

4. CONCLUSIONS

MAX-DOAS measurements of HCHO and CHOCHO have been carried out during the DANDELIONS campaign in 2005 and 2006 and successfully applied to first SCIAMACHY validation of these trace gases, adding confidence to the satellite observations. However, a more extensive validation of the satellite measurements with ground-based data from other sites is necessary. In order to confirm (or falsify) the presence of significant amounts of HCHO and CHOCHO

over the oceans, dedicated MAX-DOAS measurements from ships should be taken e.g. during latitudinal transects.

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