



Simultaneous global observations of glyoxal and formaldehyde from space

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[1] The first global simultaneous observations of glyoxal (CHOCHO) and formaldehyde (HCHO) columns retrieved from measurements by the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) satellite instrument are presented and compared to model calculations. The global pattern of the distribution of CHOCHO is similar to that of HCHO. High values are observed over areas with large biogenic isoprene emissions (Central Africa, parts of South America, and Indonesia). Also regions with biomass burning and anthropogenic pollution exhibit elevated levels of CHOCHO. The ratio of the columns of CHOCHO to HCHO is generally of the order of 0.05 in regions having biogenic emissions, which is in reasonable agreement with the current understanding of the oxidation of hydrocarbons emitted by the biosphere. However and in contrast to our model, high values of both HCHO and CHOCHO are also observed over areas of the tropical oceans. This is tentatively attributed to outflow from the continents and local oceanic biogenic sources of the precursors of HCHO and CHOCHO. **Citation:** Wittrock, F., A. Richter, H. Oetjen, J. P. Burrows, M. Kanakidou, S. Myriokefalitakis, R. Volkamer, S. Beirle, U. Platt, and T. Wagner (2006), Simultaneous global observations of glyoxal and formaldehyde from space, *Geophys. Res. Lett.*, 33, L16804, doi:10.1029/2006GL026310.

1. Introduction

[2] 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 com-

pared 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., Wiedinmyer *et al.*, 2004].

[3] Measurements of tropospheric HCHO have been made over the past three decades mainly on a campaign basis by both remote sensing and in situ techniques in urban and remote locations [e.g., Hak *et al.*, 2005 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 [Burrows *et al.*, 1999 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., Chance *et al.*, 2000; Thomas *et al.*, 1998]. Validation of HCHO columns retrieved from satellite spectra by means of aircraft measurements has been performed by [Ladstätter-Weissenmayer *et al.*, 2003; Martin *et al.*, 2004].

[4] Glyoxal, CHOCHO, the simplest alpha dicarbonyl organic compound, is formed from the oxidation of a variety of hydrocarbons [Volkamer *et al.*, 2005a; Volkamer *et al.*, 2001]. Tropospheric CHOCHO has been measured during several campaigns. For example, in the boundary layer of a rural site, Lee *et al.* [1998] and Munger *et al.* [1995] 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.* [2003] found lower values of about 0.03 ppb_v above a ponderosa pine plantation in California. [Ho and Yu, 2002] have identified CHOCHO and other aldehydes in air masses affected by biomass burning, domestic and residential log fires. In Volkamer *et al.* [2005b] 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 [Volkamer *et al.*, 2005b]. Global observations of CHOCHO from space offer the potential of identifying photochemical hot spots in the earth's atmosphere [Volkamer *et al.*, 2005b], and coupled with observations of HCHO constrain our understanding of biogenic emissions, biomass burning, and urban pollution.

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[5] Recently, the tentative identification of glyoxal in measurements from the OMI (Ozone Monitoring Instrument) satellite instrument has been reported (T. Kurosu et al., unpublished data, 2005, figures available at <http://www.cfa.harvard.edu/~tkurosu/>).

[6] In this study, the global fields of HCHO and CHOCHO were derived from the measurements of the satellite instrument SCIAMACHY using the method of Differential Optical Absorption Spectroscopy (DOAS). These data have been validated by comparison with those derived from measurements by ground-based MultiAxis DOAS, MAXDOAS, instruments. A discussion of the type and distribution of sources of CHOCHO and a comparison with a global model including HCHO and CHOCHO chemistry are presented.

2. Instruments

[7] 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 [Bovensmann et al., 1999]. SCIAMACHY was launched on ENVISAT into a sun-synchronous orbit on 1st of March 2002 and has an equator crossing time of 10 AM LT. The maximum scan width in the nadir-view is 960 km and global coverage is achieved within six days. The ground pixel size used in this study is 60 km along track by 120 km across track.

[8] Details about the MAXDOAS instruments used in this study can be found elsewhere [Wittrock et al., 2004]. Briefly, light is collected by a telescope with a moving mirror to enable near-simultaneous measurements of scattered light at multiple elevation angles. Measurements made during a recent validation campaign at Cabauw in The Netherlands and from a station located at the UNEP Buildings in Nairobi in Kenya have been used in this study.

3. Data Retrieval

[9] For the retrieval of vertical columns of HCHO and CHOCHO from the MAXDOAS and SCIAMACHY observations, the well established DOAS technique has been used. Briefly, the DOAS approach relies on the separation of narrow band absorption signatures from broad band absorption and scattering features. Retrievals comprise the determination of the slant column absorption for the gas and its conversion to a vertical column amount 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 [Wittrock et al., 2004].

[10] For the HCHO column amounts, the DOAS spectral window, the non-linear least-squares fitting procedure, and reference spectra have been developed for GOME and the ground-based instrumentation and have been described elsewhere [Heckel et al., 2005]. For the fitting of SCIAMACHY data, a spectral region of 334–348 nm was selected to avoid any correlation with an instrument grating polarisation structure around 360 nm. The AMF calculations use a priori knowledge of vertical HCHO profiles [see Wittrock, 2006].

[11] 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 [Volkamer et al., 2005c] O₃, NO₂, H₂O, O₄, a Ring spectrum, which accounts for both rotational and vibrational Raman scattering, and a quadratic polynomial are included in the fitting procedure.

[12] Almost simultaneous measurements at different viewing angles for the same solar zenith angle from the MAXDOAS instruments have been used to obtain both an accurate tropospheric column for the absorbing trace gas and profile information [Heckel et al., 2005; Wittrock et al., 2004]. The latter is used as input for the calculation of AMF for the satellite retrieval. For the satellite observations only ground scenes having less than 20 percent cloud cover are considered. Prior to conversion to vertical columns, the retrieved slant columns were normalised by assuming a mean value of $2 \cdot 10^{15}$ molec·cm⁻² for HCHO and $2 \cdot 10^{14}$ molec·cm⁻² for CHOCHO in the region between 180°W and 160°W. This normalisation is necessary for many GOME and SCIAMACHY products to compensate for offsets introduced by the solar reference measurements [Richter and Burrows, 2002].

4. Modelling Studies

[13] The 3-d global atmospheric chemistry transport model (TM) [Tsigaridis and Kanakidou, 2003] was used for the comparison with the observations of HCHO and CHOCHO. TM is forced by ECMWF meteorology and is able to simulate all major aerosol components together with the gas phase chemistry of the troposphere. The applied model version (TM4-ECPL) has a horizontal resolution of 4° in latitude and 6° in longitude and 31 vertical layers. It describes C₁–C₅ hydrocarbon chemistry including isoprene [Poisson et al., 2000] and lumped terpenes and aromatic hydrocarbon chemistry [Tsigaridis and Kanakidou, 2003]. In the model, CHOCHO is formed during the oxidation of ethene and isoprene and destroyed by photolysis, reaction with OH radicals and dry deposition. HCHO is produced from all hydrocarbons oxidation and removed from the troposphere by reactions with OH and NO₃ radicals, photolysis and dry and wet deposition. Terpenes and other reactive organics, like sesquiterpenes and terpenoid alcohols, produce glyoxal since their chemistry is partially lumped on isoprene as described by Tsigaridis and Kanakidou [2003]. Annual biogenic emissions of 400 Tg isoprene and 202 Tg terpenes and other reactive biogenic organics as well as 2 Tg HCHO primary anthropogenic emissions are adopted in the model whereas any primary glyoxal emissions have been neglected. Results from the 2005 simulations are presented.

5. Results and Discussion

[14] The retrieval of HCHO from space using GOME data has been reported previously [e.g., Thomas et al., 1998]. To demonstrate the detection of CHOCHO from the SCIAMACHY observations, Figure 1 shows exemplarily a fitting result. In Figures 2a and 2b, the first global annual composite of the CHOCHO and HCHO retrieved from SCIAMACHY for the year 2005 are depicted. En-

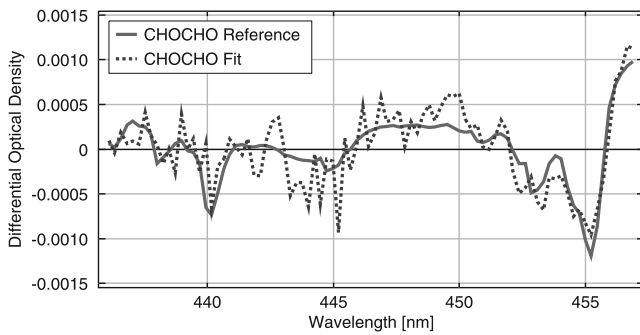


Figure 1. Example of a DOAS fit for glyoxal using SCIAMACHY data (orbit 40711083). The solid line is the scaled laboratory reference for CHOCHO, the dotted line the fit result after removing all other absorbers and a polynomial. The slant column, in this case, is 4.2×10^{15} molec/cm².

hanced CHOCHO column amounts of $\geq 1 \cdot 10^{15}$ molec·cm⁻² 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 is found over the tropical rain forests and in regions having regular biomass burning events, for example in Ghana. In Asia, large values of CHOCHO 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 common main sources.

[15] CHOCHO column amounts retrieved over water are influenced by interference from liquid water absorption. This can lead to negative values above clear water regions. Inclusion of a liquid water reference spectrum in the fitting procedure for water ground scenes reduces these artefacts. Nevertheless, measurements over water have to be inter-

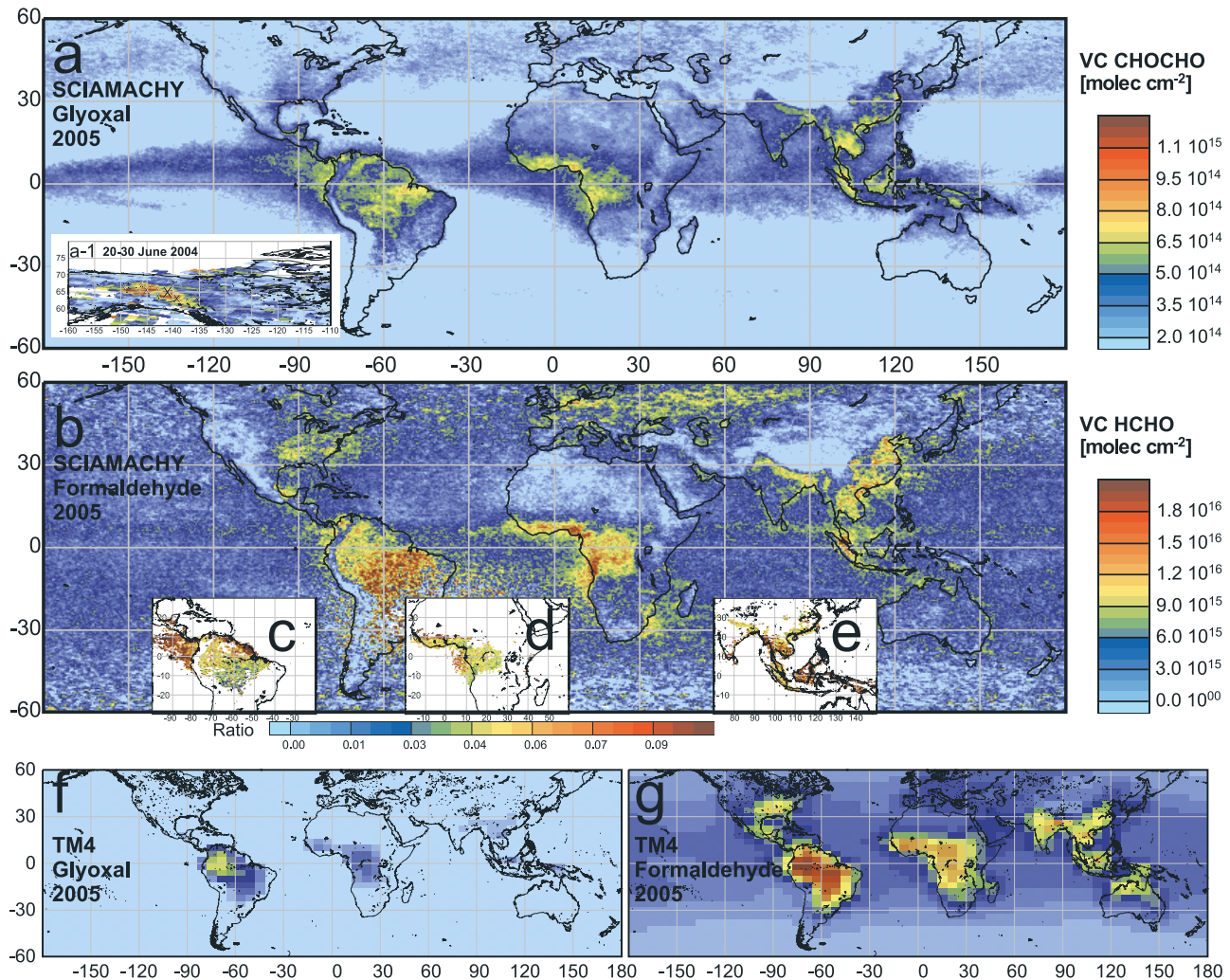


Figure 2. Yearly mean for (a) glyoxal and (b) formaldehyde derived from SCIAMACHY observations in 2005. (c–e) Sub-figures illustrate the ratio between measured CHOCHO and HCHO while (f–g) show the global distribution as calculated by the model. In (Figure 2a (inset)), CHOCHO is shown during biomass burning in Alaska in June 2004. The area with biomass burning is marked with X signs applying distributions from AATSR (Advanced Along Track Scanning Radiometer) fire counts.

Table 1. Comparison Between SCIAMACHY (SCIA) and MAXDOAS (MAX) HCHO and CHOCHO Columns at the Measurement Sites Nairobi and Cabauw^a

	Nairobi, 1°S, 37°E				Cabauw, 52°N, 5°E			
	CHOCHO, 10 ¹⁴		HCHO, 10 ¹⁵		CHOCHO, 10 ¹⁴		HCHO, 10 ¹⁵	
	molec·cm ⁻²		molec·cm ⁻²		molec·cm ⁻²		molec·cm ⁻²	
	SCIA	MAX	SCIA	MAX	SCIA	MAX	SCIA	MAX
April 2005	2.8	3.6	4.0	5.5	-	-	-	-
May 2005	2.8	3.4	-	-	3.5	3.8	7.1	4.9
June 2005	2.7	2.4	4.1	5.1	3.2	4.1	8.2	7.0
July 2005	1.3	2.0	4.7	4.5	3.4	3.7	5.1	5.1
Error	2.0	1.0	2.5	1.0	2.0	0.8	2.5	0.8

^aThe last row gives estimated errors on the monthly means calculated from about 10 (SCIAMACHY) to 20 (MAXDOAS) single measurements.

preted with care. Several regions above the oceans display significantly elevated CHOCHO amounts (Figure 2a), including biologically active regions: for example, near the equator, over the Indian Ocean and close to the coast of China. As is the case for HCHO, the Pacific region between the Galapagos Islands and the coast of Colombia exhibit large amounts of CHOCHO of up to $8 \cdot 10^{14}$ molec·cm⁻². This is potentially due to the outflow of terrestrial sources of the VOC precursors of HCHO and CHOCHO and the possible presence of biogenic VOC sources over the biogenically active oceanic regions. In this context, *Warneck* [2005] has pointed out in a box model study that glyoxal is a prominent oxidation product from, for example, acetylene and ethene in the marine troposphere.

[16] In the global composite maps of HCHO and CHOCHO, the regions with large biogenic emissions have the largest local column amounts. However, for selected areas and time periods, biomass burning also produces significant amounts of CHOCHO. This is illustrated in Figure 2a (inset), which shows CHOCHO columns during a biomass burning event in Alaska in June 2004. Significant amounts of CHOCHO were found and correlate well with fire counts.

[17] A validation of the retrieved column amounts of HCHO and CHOCHO from SCIAMACHY observations has been performed using MAXDOAS observations. First results (Table 1) indicate agreement within experimental accuracy. Clearly, more validation measurements are needed in particular in regions with large columns and over the oceans.

5.1. Ratio Between CHOCHO and HCHO

[18] The ratio of CHOCHO to HCHO is determined by the relative contributions of the different sources to the two trace species. According to *Spaulding et al.* [2003] and *Munger et al.* [1995], a ratio of 0.04 to 0.06 is expected for biogenic emissions of, for example, isoprene but is larger for sources with larger contributions from aromatic hydrocarbons [*Volkamer et al.*, 2005a]. In Figures 2c–2e, the ratio derived from SCIAMACHY data is plotted for three different regions using only CHOCHO columns above a threshold of $5 \cdot 10^{14}$ molec·cm⁻² to avoid large scatter for ratios at low columns, which are dominated by measurement noise. Overall, the range of ratios found in this study is of the order as the predicted values for isoprene emissions, supporting the current assumptions for CHOCHO formation. However, locally, significantly higher values are found, for example,

above Indonesia and India, most likely resulting from additional formation mechanisms for CHOCHO.

5.2. Comparison With Model Results

[19] The TM4-ECPL model computes column distributions of CHOCHO and HCHO (Figures 2f–2g) that are similar to those derived from SCIAMACHY. The model calculated annual mean values maximize in the tropics for both compounds over biogenic emission areas with columns exceeding $12 \cdot 10^{15}$ molec·cm⁻² for HCHO and $0.8 \cdot 10^{15}$ molec·cm⁻² for CHOCHO. However, the model does not capture the enhancement of CHOCHO columns over the tropical ocean seen in SCIAMACHY observations, although it simulates reasonably well the tropical enhancement of HCHO. This may indicate the existence of primary or secondary tropical sources of CHOCHO that are neglected in the model. The ratio of the simulated CHOCHO to HCHO has its highest values over continental areas in the tropics (up to 0.04) and over the mid latitudes (ratios up to 0.024). These ratios are smaller than observed by SCIAMACHY and this is probably best explained by missing sources or an inadequate chemical description of the formation of CHOCHO in the model.

6. Conclusions

[20] The first global observations of HCHO and CHOCHO using measurements of the SCIAMACHY instrument have been presented and discussed. The global pattern of CHOCHO columns was found to be similar to that of HCHO, indicating common atmospheric sources in particular isoprene. The ratio between CHOCHO and HCHO was found to be about one to twenty in source regions such as the tropical rain forests, similar to predictions. At some locations, larger ratios are found and this is attributed to unidentified additional sources of CHOCHO. A comparison of the columns retrieved from SCIAMACHY measurements with MAXDOAS data at two locations shows good agreement within estimated uncertainties. Further validation at a broad variety of locations is recommended. Large CHOCHO columns are found primarily over areas having strong biogenic emissions in the tropics which appear to be the dominant global source. This is confirmed by a 3-d global CTM, which simulates the observed CHOCHO annual mean column reasonably well. During strong biomass burning events CHOCHO can also be clearly observed as demonstrated for fires in Alaska. More detailed comparisons between measurements and model results, coupled with retrievals of other trace gases such as NO₂, will constrain our knowledge of VOC chemistry in the current generation of atmospheric models.

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