

The influence of natural and anthropogenic secondary sources on the glyoxal global distribution

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Abstract. Glyoxal, the smallest dicarbonyl, which has recently been observed from space, is expected to provide indications on volatile organic compounds (VOC) oxidation and secondary aerosol formation in the troposphere. Glyoxal (CHOCHO) is known to be mostly of natural origin and is produced during biogenic VOC oxidation. However, a number of anthropogenically emitted hydrocarbons, like acetylene and aromatics, have been positively identified as CHOCHO precursors. The present study investigates the contribution of pollution to the CHOCHO levels by taking into account the secondary chemical formation of CHOCHO from precursors emitted from biogenic, anthropogenic and biomass burning sources. The impact of potential primary land emissions of CHOCHO is also investigated. A global 3-dimensional chemistry transport model of the troposphere (TM4-ECPL) able to simulate the gas phase chemistry coupled with all major aerosol components is used.

The secondary anthropogenic contribution from fossil fuel and industrial VOCs emissions oxidation to the CHOCHO columns is found to reach 20–70% in the industrialized areas of the Northern Hemisphere and 3–20% in the tropics. This secondary CHOCHO source is on average three times larger than that from oxidation of VOCs from biomass burning sources. The chemical production of CHOCHO is calculated to equal to about 56 Tg y⁻¹ with 70% being produced from biogenic hydrocarbons oxidation, 17% from acetylene, 11%

from aromatic chemistry and 2% from ethene and propene. CHOCHO is destroyed in the troposphere primarily by reaction with OH radicals (23%) and by photolysis (63%), but it is also removed from the atmosphere through wet (8%) and dry deposition (6%). Potential formation of secondary organic aerosol through CHOCHO losses on/in aerosols and clouds is neglected here due to the significant uncertainties associated with the underlying chemistry. The global annual mean CHOCHO burden and lifetime in the model domain are estimated to be 0.02 Tg (equal to the global burden seen by SCIAMACHY over land for the year 2005) and about 3 h, respectively. The model results are compared with satellite observations of CHOCHO columns. When accounting only for the secondary sources of CHOCHO in the model, the model underestimates CHOCHO columns observed by satellites. This is attributed to an overestimate of CHOCHO sinks or a missing global source of about 20 Tg y⁻¹. Using the current primary emissions of CHOCHO from biomass burning together with the anthropogenic combustion sources of about 7 Tg y⁻¹ leads to an overestimate by the model over hot spot areas.

1 Introduction

In the presence of nitrogen oxides (NO_x=sum of nitrogen oxide, NO, and nitrogen dioxide, NO₂), the photochemical degradation of volatile organic compounds (VOCs) leads to secondary gaseous and particulate products, such as ozone (O₃) and secondary organic aerosols (SOA) that are



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important contributors to the “photochemical smog” (see e.g. Poisson et al., 2000; Kanakidou et al., 2005). Air pollution has severe negative effects on human health (Evans et al., 2002; Pope and Dockery, 2006), ecosystems (Gregg et al., 2003) and regional climate (Ramanathan and Crutzen, 2003). The improvement of our understanding of air quality in urban areas requires a detailed knowledge of the sources, sinks and distributions of the all pollutants including VOCs. There are a large number of VOC compounds and their degradation in the troposphere is complex. However, relatively small molecules, such as formaldehyde (HCHO), methylvinylketone (MVK) and O₃ are formed during the degradation of many VOC. The amounts and distribution of these gases are determined by both anthropogenic and natural emissions and can be measured in the troposphere.

Recent studies have shown that glyoxal (CHOCHO), the simplest alpha dicarbonyl organic compound, is one of the most prevalent dicarbonyls in the atmosphere. The main primary sources of glyoxal result from biofuel burning (Hays et al., 2002) and vehicle emissions (Kean et al., 2001; Grosjean et al. 2001), but our knowledge of these sources is highly uncertain due to the large variability of emission factors and the scarcity of the available observations. Rates of CHOCHO emissions from biofuel burning have been reported to be 2 to 5 times higher than those of HCHO (Hays et al., 2002). During the MCMA-2003 campaign in Mexico City, time-resolved direct observations of CHOCHO showed no accumulation of CHOCHO during rush-hour, but a fast rise in CHOCHO concentrations after the onset of photochemical activity, indicating that ambient CHOCHO is dominated by VOC photochemical sources. Recent studies have demonstrated that glyoxal is a useful indicator molecule for VOC oxidation processes (Volkamer et al., 2005b).

CHOCHO is produced via the oxidation of C_n-hydrocarbons, where $n \geq 2$ (Calvert et al. 2000; Calvert et al. 2002), emitted as a result of anthropogenic activity, biogenic processes and biomass burning sources. It is a first generation product of acetylene oxidation by hydroxyl radical (OH) and is produced from the oxidation of a number of other unsaturated VOCs by O₃ and OH, including ethene, C₂H₄, and isoprene, CH₂=C(CH₃)CH=CH₂ (for a compilation of glyoxal precursor VOCs see Volkamer et al., 2005a, and Volkamer et al., 2007, and references therein). Similarly CHOCHO has been identified as a first generation product of the aromatic ring-opening routes during the OH radical initiated oxidation of aromatic hydrocarbons (Volkamer et al., 2001, and references therein). The secondary production of CHOCHO from the atmospheric degradation of furanones, unsaturated γ -dicarbonyls and phenols has been observed to be negligible (Volkamer et al., 2001; Bloss et al., 2005). The CHOCHO formation from isoprene, globally the largest source for secondary CHOCHO, mostly proceeds via the further oxidation of the intermediates like glycolaldehyde and C₅-hydroxycarbonyls (Saunders et al., 2003), which are generated in the oxidation of isoprene.

CHOCHO has also been detected in atmospheric aerosols (Kawamura et al., 1996; Matsunaga et al., 2003; Liggio and McLaren, 2003; Garcia-Alonso et al., 2006). It has been suggested that CHOCHO is strongly involved in the formation of secondary organic aerosol, SOA, in the troposphere by participating in heterogeneous reactions that form organic sulfate compounds (Liggio et al., 2005a). CHOCHO is more reactive with respect to hydration, polymerization and acetal/hemiacetal formation in the presence of alcohols than most other aldehydes (Jang and Kamens, 2001). Based on kinetic studies by Liggio et al. (2005b), the amount of SOA potentially formed by CHOCHO could be large enough to account for a significant part of the missing SOA in the low and free troposphere currently not reproduced by models (Heald et al., 2005; Volkamer et al., 2006a). Laboratory measurements consistently find evidence for SOA formation from CHOCHO (Liggio et al., 2005a; 2005b; Kroll et al., 2005) but are inconclusive as to the atmospheric relevance as a SOA source. Recent first field evidence of a missing CHOCHO sink is consistent with the upper values of SOA formation from CHOCHO (Volkamer et al., 2007) and supports the atmospheric relevance of this process.

CHOCHO absorbs in the UV and visible spectral range between 200 and 470 nm with two strong absorption features: a broad UV band between 220 and 350 nm and a more structured band between 350 and 470 nm (Atkinson et al., 2006 and references therein). The spectrum between 425 and 457 nm includes a sharp peak of CHOCHO at 455 nm (Volkamer et al., 2005c) and several minor features. These structures have been used in the recent direct detection of CHOCHO at local scales (Volkamer et al., 2005b; Sinreich et al., 2007) and global scales (Wittrock et al., 2006) from the measurements of the SCIAMACHY satellite instrument using the well established Differential Optical Absorption Spectroscopy (DOAS) technique.

Simultaneous observations of HCHO, CHOCHO, carbon monoxide (CO) and NO₂ have been proposed to provide insight to the contribution of photochemistry versus that of primary sources to the building up of pollutants in the troposphere (Garcia-Alonso et al., 2006). HCHO, which has previously been used as an indicator of VOC oxidation (Palmer et al., 2003; Wittrock et al., 2006), is produced in the oxidation of methane and other VOC. However, over urban hot spot areas, HCHO levels are determined by both direct emissions and photochemical oxidation of VOCs. Observations show that the ambient levels of CHOCHO are about 10 times less affected by primary sources than HCHO (as argued in Volkamer et al., 2005b). CHOCHO is therefore a valuable indicator of VOC oxidation processes (Volkamer et al., 2005b) and particularly of fast photochemistry of anthropogenic VOCs (Spaulding et al., 2003). CO is a tracer of primary anthropogenic emissions (Garcia-Alonso et al., 2006). Garcia et al. (2006) used the CHOCHO-CO tracer pair for source apportionment of ambient HCHO and found that 40–70% (depending on the time of day) of the ambient HCHO

was emission-related in Mexico City. Furthermore, the ratio of CHOCHO to NO₂ provides insight into the photochemical age of the studied air mass since it is increasing with air mass age and conversion of NO₂ to nitric acid that is further removed from the atmosphere (Volkamer et al., 2005b; Sinreich et al., 2007).

In the present study, a global 3-dimensional chemistry transport model of the troposphere TM4-ECPL is used in order to investigate CHOCHO formation from biogenic, biomass burning and anthropogenic precursors and its seasonal variability. The model results are compared with satellite observations from the SCIAMACHY instrument taken in 2005. A potential primary anthropogenic source of CHOCHO is also investigated. Finally, the utility of synergistic use of CHOCHO and other short-lived trace gases observations from space to distinguish between the impact of anthropogenic and of natural emissions on tropospheric chemistry is examined.

2 Model description

The model used for the present study is the well documented off-line chemical model TM4 (Noije et al., 2004, 2006). TM4 has been evaluated in the frame of some intercomparison exercises (Shindell et al., 2006; Stevenson et al., 2006). It has 31 vertical hybrid layers from the surface to 10 hPa and can run in two different horizontal resolutions, the low resolution of 6°×4° in longitude and latitude and the high resolution of 3°×2°. For the present study, the low resolution version of the model has been used mainly for the source apportionment analysis. The basic simulation has been also performed with the high resolution version TM4-ECPL to investigate the impact of grid size on the calculated CHOCHO columns. The model's input meteorology comes from the ECMWF operational data for 2005 and is updated every 6 h.

2.1 Emissions

The adopted emissions of primary particles (carbonaceous aerosols, dust, sea-salt, small fraction of sulfate) in TM4-ECPL are presented in detail by Tsigaridis et al. (2006) and Tsigaridis and Kanakidou (2007). For the biogenic VOC emissions TM4-ECPL uses the 1°×1° gridded emission distribution from the POET database (Granier et al., 2005) that is based on the GEIA (Guenther et al., 1995) inventory. For the anthropogenic VOC, NO_x and CO emissions, TM4-ECPL also uses the POET emission database. This corresponds to the year 2000 that is the most recent year with complete information available. The POET dataset is derived from the Emission Database for Global Atmospheric Research (EDGAR) version 3 inventories for the anthropogenic emissions for the year 1995 with appropriate modifications to refer to recent years (Olivier et al., 2003; Granier et al., 2005). As a result of differences in the rep-

resentation of the VOC chemistry in TM4-ECPL used for this study compared to the earlier studies by Tsigaridis and coworkers, TM4-ECPL uses a different speciation in the VOC emissions. The present study considers annual biogenic VOC emissions of 501 Tg of isoprene (1 Tg from the oceans) and 244 Tg of monoterpenes and Other Reactive Volatile Organic Compounds (ORVOC) that are able to produce aerosols, such as sesquiterpenes, terpenoid alcohols etc, as discussed in Griffin et al. (1999) and incorporated in the model as explained in Kanakidou et al. (2000). Additional biogenic emissions of oxygenated organics not considered as aerosol precursors are those of acetone, CH₃COCH₃, methanol, CH₃OH, acetaldehyde, CH₃CHO, and other light carbonyls (27 Tg y⁻¹, 243 Tg y⁻¹, 2 Tg y⁻¹ and 14 Tg y⁻¹, respectively), which are also taken into account in the model. HCHO emissions from biomass burning and anthropogenic activities of 2.5 Tg y⁻¹ and 1.3 Tg y⁻¹, respectively, are also considered (POET database). The impact of potentially significant anthropogenic primary sources of CHOCHO on its tropospheric column amounts has been investigated in one simulation that considers biomass burning and other anthropogenic combustion primary CHOCHO emissions to be 4.8 and 2.5 Tg y⁻¹ respectively, i.e. almost 2 times (within the range given by Hays et al., 2002) higher than those of HCHO. The adopted emissions of aromatic hydrocarbons (POET dataset) total 33 Tg y⁻¹ with about 7% emitted from biomass burning, and in TM4-ECPL consist of 7 Tg y⁻¹ of benzene, 14 Tg y⁻¹ of toluene and 12 Tg y⁻¹ of xylene. Among the other compounds of interest for the present study, ethene, propene and acetylene emissions from the same database account for 17 Tg y⁻¹, 7 Tg y⁻¹ and 7 Tg y⁻¹, respectively. A table with the global annual emissions used in TM4-ECPL for the present study is given in the Supplementary material <http://www.atmos-chem-phys.net/8/4965/2008/acp-8-4965-2008-supplement.pdf>.

2.2 Chemistry

The model considers sulphur, ammonia and C₁-C₅ hydrocarbon chemistry including isoprene, as well as highly simplified terpenes and aromatics chemistry. It uses an updated version of the Kanakidou and Crutzen (1999) and Poisson et al. (2000) chemical mechanism suitable to simulate the chemistry of the global troposphere. Gas-phase chemistry and secondary aerosol formation are coupled and computed on-line together with all other major aerosol components (sulphate, nitrate, ammonium, carbonaceous, dust, sea-salt, aerosol water). For the present simulations, dust and sea-salt components have been neglected in order to save computing time. The VOC scheme explicitly considers methane, ethane, ethene, acetylene, propane, propene, butane and isoprene. Reactions of monoterpenes and aromatics are affecting both gas-phase chemistry and aerosol production as described in Tsigaridis and Kanakidou (2003, 2007). Monoterpenes and ORVOC are represented by α - and β -pinene, while

Table 1. Reactions taken into account in the TM4-ECPL model and describing CHOCHO production and destruction and the references for the rate coefficients, k , used in the model.

a)			
Number	Reactions (Gas phase chemical production)	k	Reference
1	Isoprene+OH→0.03CHOCHO+products	$2.7 \text{ E-}11 \exp(390/T)$	IUPAC (2006)
2	$\text{C}_2\text{H}_4+\text{O}_3+2\text{O}_2\rightarrow 0.0044\text{CHOCHO+products}$	$9.1 \text{ E-}15 \exp(-2580/T)$	IUPAC (2006)
3	$\text{C}_3\text{H}_6+\text{O}_3+2\text{O}_2\rightarrow 0.05\text{CHOCHO+products}$	$5.5 \text{ E-}15 \exp(-1880/T)$	IUPAC (2006)
4	$\text{C}_2\text{H}_2+\text{OH}\rightarrow 0.635\text{CHOCHO+products}$	3 bodies reaction	IUPAC (2006)
5	Benzene+OH→0.36CHOCHO+products	$2.47 \text{ E-}12 \exp(207.0/T)$	Calvert et al. (2002)
6	Toluene+OH→0.306CHOCHO+products	5.96 E-12	Atkinson (1994)
7	Xylene+OH→0.319CHOCHO+products	1.72 E-11	Average of ortho-, meta-, para-isomers
8	$\text{HOCH}_2\text{CHO+OH+O}_2\rightarrow \text{CHOCHO+HO}_2+\text{H}_2\text{O}$	2.2 E-12	IUPAC (2006)
b)			
Number	Reactions (Gas phase chemical destruction)	k	Reference
1	$\text{CHOCHO+OH}\rightarrow 2\text{CO+HO}_2+\text{H}_2\text{O}$	$2.8 \times 10^{-12} \exp(340/T)$	Feierabend et al. (2008)
2	$\text{CHOCHO+NO}_3+\text{O}_2\rightarrow \text{HNO}_3+\text{HO}_2+2\text{CO}$	1.2 E-15	upper limit estimate by I. Barnes (personal communication, 2007)
3	$\text{CHOCHO}+h\nu\rightarrow 2\text{HO}_2+2\text{CO}$	J_{CHOCHO}	IUPAC (2006)

aromatic compounds are represented by benzene, toluene and xylene. The α - and β -pinene oxidation by hydroxyl (OH) and nitrate (NO_3) radicals and ozone are considered to form semi-volatile organics, which are the precursors of SOA, and C_5 peroxy radicals, like the first generation peroxy radicals from isoprene oxidation. The reactions of all peroxy radicals with hydrogen peroxide (HO_2) and methyl peroxide (CH_3O_2) are taken into account as indicated in Vrekoussis et al. (2004) with updated kinetics based on Atkinson et al. (2006). NO_3 radical reactions with aldehydes, alcohols, dimethylsulfide, CH_3SCH_3 (DMS), butane, C_4H_{10} , and unsaturated hydrocarbons are considered. Aromatics are considered to react with OH, O_3 and NO_3 , with the reaction of OH being the dominant removal process accounting for 100, 99.9, 99.8% of the removal of benzene, toluene and xylene, respectively. The reactions of aromatics with OH produce CHOCHO as a first generation product and peroxy radicals that can further react to form gaseous and aerosol products. For simplicity purposes, their gaseous products are treated in the model as butyloperoxy radicals and attention is paid to preserve the carbon balance. SOA production by VOC oxidation is parameterized as detailed in Tsigaridis and Kanakidou (2003). The full list of chemical reactions and reaction rates adopted in TM4-ECPL is given in the Supplementary material <http://www.atmos-chem-phys.net/8/4965/2008/acp-8-4965-2008-supplement.pdf>.

For CHOCHO, the TM4-ECPL model considers primary formation during the oxidation of isoprene, acetylene, aromatic hydrocarbons (Volkamer et al., 2005a) and ozonolysis of ethene and propene as well as secondary formation (via glycolaldehyde – HOCH_2CHO) from the oxidation of ethene and from peroxy radicals produced during the oxida-

tion of isoprene (Table 1). Other biogenic hydrocarbons, like terpenes, and other reactive organics, like sesquiterpenes, and terpenoid alcohols also produce CHOCHO (as secondary product) in TM4-ECPL, since their chemistry is lumped on the first generation peroxy radicals of isoprene (as parameterized in Tsigaridis and Kanakidou, 2003). CHOCHO is destroyed by photolysis (Volkamer et al., 2005c; Atkinson et al., 2006; Tadic et al., 2006), reaction with OH (Feierabend et al., 2008) and to a lesser extent with NO_3 , and removed via wet and dry deposition. For the dry deposition of CHOCHO as for the other gaseous species, the Ganzeveld and Lelieveld (1995) resistance-in-series scheme has been used, which is based on the formulation developed by Wesely (1989). For the wet deposition, both large scale and convective precipitation are considered and the in-cloud and below cloud scavenging are parameterised in the model TM4-ECPL as described in detail by Jeuken et al. (2001). In-cloud scavenging of CHOCHO is parameterized based on the Henry's law coefficient of $K_H=2.6 \cdot 10^7 \text{ M} \cdot \text{atm}^{-1}$ (Kroll et al., 2005) that is 2 orders of magnitude higher than the Henry's Law coefficient suggested by Lim et al. (2005). The in-cloud loss of CHOCHO has been suggested to be a significant sink for glyoxal leading to SOA formation (Liggio et al., 2005; Loeffler et al., 2006; Sorooshian et al., 2007). The importance of this process for SOA budget in the global troposphere requires further investigation by targeted 3-dimensional simulations.

2.3 The simulations

In order to investigate the influence of natural and anthropogenic emissions of hydrocarbons on CHOCHO

distribution and its global budget, several different CHOCHO-chemistry scenarios have been considered. The first simulation (S1) accounts for CHOCHO production only from the oxidation of the naturally emitted VOCs. S1 also considers in-cloud loss of CHOCHO as explained in Sect. 2.2. The second simulation (S2) is the same as that for S1 but also takes into account the contribution of biomass burning emissions of ethene, propene, acetylene and aromatics to the chemical production of CHOCHO. The third simulation (S3, used as the base case for the present study) is as (S2) but considers in addition the contribution of anthropogenic emissions of ethene, propene, acetylene and aromatics to CHOCHO formation, i.e. accounts for all known photochemical sources of glyoxal. This simulation has also been performed at the high horizontal resolution of TM4-ECPL (S3-H). The difference between the simulations (S2) and (S1) is attributed to the secondary production of glyoxal from the biomass burning VOCs; whereas that between (S3) and (S2) is attributed to the production of glyoxal from anthropogenic VOC. Despite the significant variability in the primary CHOCHO emission factors and the scarcity of available data, the possible impact of significant primary sources of CHOCHO on its tropospheric columns has been investigated in an additional simulation (S4) that considers such emissions from biomass burning as well as from anthropogenic combustion sources proportional to those of HCHO (see also Sect. 2.1). Finally, the impact of the assumption of a lower Henry's law coefficient (K_H) for CHOCHO wet removal on its tropospheric burden has been investigated by an additional simulation (S5) that uses a 100 times lower K_H than the other simulations.

When compared with our earlier work (Wittrock et al., 2006), simulation S3 of the present study i) uses updated anthropogenic and biomass burning emission inventories based on the POET database for the year 2000 and about 20% higher isoprene emissions of 500 Tg yr^{-1} , which are within the range of the present-day estimates by Guenther et al. (2006), ii) takes into account the formation of CHOCHO from ethene, propene, acetylene and aromatics that are predominantly of anthropogenic origin but have also a minor natural component, iii) takes into account the temperature dependence of the reaction of CHOCHO with OH radicals (Feierabend et al., 2008), and iv) calculates on line as described by Landgraf and Crutzen (1998) and Lelieveld et al. (2002) the photolysis rates of CHOCHO based on the IUPAC and JPL recommendations (Atkinson et al., 2006 and references therein; Sander et al., 2006). Moreover, Wittrock et al. (2006) used diurnal mean CHOCHO columns to compare with the satellite observations whereas in the present study the columns calculated for the satellite overpass time have been used (10–11 a.m. local time).

3 Satellite observations

3.1 The instrument

The sensor SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CartographY) is mounted on the ESA ENVISAT satellite. It is designed to measure sunlight transmitted, reflected and scattered by the earth's atmosphere or surface in the ultraviolet, visible and near infrared (Burrows et al., 1995; Bovensmann et al., 1999). The sun-synchronous, near polar orbit of the satellite has a local equator crossing time of 10 a.m. in the descending node. The alternative measurements of nadir and limb viewing geometries (Gottwald et al., 2006) are coupled with a swath width of 960 km and global coverage is achieved within six days. The ground pixel size used in this study is 30 km along track by 60 km across track.

3.2 The retrieval technique and CHOCHO algorithm

The retrieval approach adopted for the vertical columns of CHOCHO is based on the well established DOAS technique. Briefly, DOAS is used for the determination of the Slant Column densities (SCD) of the respective absorbers in a given spectral window (436–457 nm for the present study). Only ground scenes having less than 20 percent cloud cover are considered. The SCD is then converted to Vertical Column Densities (VCD) by applying the air mass factor (AMF), which is defined as the ratio of the SCD/VCD. This accounts for the path of light through the atmosphere and considers the vertical profiles of scattering and absorbing species (Wittrock et al., 2004). The absorption cross sections of CHOCHO (Volkamer et al., 2005c), O_3 , NO_2 , H_2O , O_4 , phytoplankton (Bracher and Tilzer, 2001; Vountas et al., 2007), a ring spectrum, which accounts for rotational Raman scattering, and a quadratic polynomial are included in the fitting procedure.

Prior conversion to vertical columns, the retrieved slant columns are normalised by assuming a mean value of $0.5 \cdot 10^{14} \text{ molecules.cm}^{-2}$ for CHOCHO over the Pacific in latitudes ($30^\circ \text{ N} - 30^\circ \text{ S}$) in the region between 165° E and 165° W . This normalisation is necessary for many GOME and SCIAMACHY products to compensate for offsets introduced by the solar reference measurements and interference from other absorbers (Richter and Burrows, 2002). More details on the CHOCHO analysis can be found in (Wittrock et al., 2006). For comparison with the global model, the SCIAMACHY data, which initially are gridded to $0.125^\circ \times 0.125^\circ$, have been re-gridded to the horizontal resolution of the model. This data manipulation could justify the anomalous high values of CHOCHO near a few ice/water borders shown in Fig. 1.

Table 2. TM4-ECPL model calculations of CHOCHO (S3-S3H; range of seasonal values for the low and high resolution simulations; S4: seasonal mean values and standard deviation) and comparisons with ground based observations. Observations are associated with an error of at least $\pm 15\%$.

Location	Coordinates	Period	Model (S3-S3H) (ppbv)	Model (S4) (ppbv)	Observations (ppbv)	Reference
Pinnacles, Shenandon National Park	36.29 N 121.10 W	Autumn	0.04–0.13	0.06 \pm 0.01	0.04	Munger et al. (1995)
Georgia, USA	32.32 N 82.08 E	Summer	0.02–0.03	0.02 \pm 0.01	0.02–0.09	Lee et al. (1995)
Long Beach, Central LA, Azusa, Claremont, USA	33.4 N 118.11 W (mean)	Autumn	0.07–0.14	0.09 \pm 0.03	0.78 \pm 0.85	Grosjean et al. (1996)
Porto Allegre, Brazil	30.2 S 51.1 W	Spring	0.02–0.08	0.02 \pm 0.01	0.30	Grosjean et al. (1999)
Los Angeles, USA	34.3 N 118.15 W	Autumn	0.02–0.07	0.09 \pm 0.03	0.04–0.95	Kawamura et al. (2000)
Giesta, Portugal	41.11 N 8.35 E	Summer	0.01	0.01	0.52–2.42	Borrego et al. (2000)
Las Vegas, USA	36.10 N 115.12 W	Summer Winter	0.11–0.17 0.02–0.11	0.18 \pm 0.5 0.14 \pm 0.01	0.12–0.42 0.09–0.21	Jing et al. (2001)
Hong Kong, China	22.18 N 114.1 E	Winter	0.05–0.06	0.09 \pm 0.03	19.70–28.0 8.40–23.7 8.60–11.9 8.80–14.8	Ho and Yu (2002)
Pabsthum (near Berlin), Germany	52.51 N 12.56 E	Summer	0.18 \pm 0.03	0.17 \pm 0.03	0.01–0.12	Moortgat et al. (2002)
Mexico City, Mexico	19.24 N 99.12 W	Spring	0.21–0.41	0.35 \pm 0.13	0.15–1.82	Volkamer et al. (2005)
MIT, USA	42.36 N 71.09 W	Summer	0.19–0.41	0.18 \pm 0.03	0.04–0.14	Sinreich et al. (2007)
ICARTT 2004 RV Ron Brown	43 N 68 W	Summer	0.14–0.19	0.18 \pm 0.03	0.10–0.35	Sinreich et al. (2007)

4 Results and discussion

4.1 Comparison of CHOCHO from model and surface observations

Even at its high spatial resolution of 2° latitude and 3° longitude, TM4-ECPL has a rather coarse grid that at 45° N corresponds to about 220 km in latitude \times 230 km in longitude. Therefore, it is expected that as most global models, TM4-ECPL underestimates short lived species concentrations over hot spot areas. This is because these hot spot areas extend only over a small fraction of the surface of the model grid boxes and thus in these model grids the short lived species are artificially diluted over hot spot areas by instantaneous mixing with cleaner air from the surrounding locations in the same grid boxes. Keeping in mind these limitations, the re-

sults of the high resolution TM4 simulation (S3-H) are evaluated by comparison with ground based observations reported in the literature for different places of the world (Table 2). An overall reasonable agreement is seen between the TM4-ECPL S3-H simulated boundary layer CHOCHO concentrations and the surface observations. The model reproduces well the observations by Sinreich et al. (2007) at coastal oceanic areas on board the RV Ron Brown. In contrast, it misses the extremely high values observed inside the urban core of Hong Kong by Ho and Yu (2002).

In addition to the above mentioned spatial effects that contribute to the differences between model results and observations, uncertainties in oxidant fields, VOC loadings and particulate matter levels are also at the origin of differences illustrated in Table 2. The use of emission inventories for the year 2000 to simulate the year 2005 can also cause some

discrepancies. In addition, potentially existent primary CHOCHO sources that have been neglected in TM4-ECPL (as discussed in Sect. 2.3) could be a reason for an underestimation of CHOCHO levels by simulation S3. However, results from the simulation S4 that accounts for some potential primary sources of CHOCHO are also reported in Table 2 and indicate only minor improvement in the model comparisons with surface observations. On the other hand, a potentially strong missing sink of CHOCHO could explain an overestimate of CHOCHO in the model. Such a sink of CHOCHO on aerosols has been suggested by Volkamer et al. (2007) to reconcile glyoxal observations in Mexico City with results of a box model that was very well experimentally constrained.

It has to be stressed that there is a clear need for more ground based CHOCHO observations available for model and satellite evaluations, in particular over oceanic areas since most of the CHOCHO observations are restricted to continental anthropogenically influenced locations.

4.2 Annual mean CHOCHO columns

Focusing on the global annual mean CHOCHO column distribution for the year 2005, the S3-H simulations are compared with the columns retrieved from SCIAMACHY measurements in Fig. 1. The model (Fig. 1a) captures high columns of CHOCHO in the tropics associated mainly with biogenic and biomass burning emissions, in agreement with the retrievals based on SCIAMACHY measurements (Fig. 1b), although the model underestimates the observations.

As seen in the figures, the current version of TM4-ECPL does not reproduce the significant amounts of CHOCHO retrieved from SCIAMACHY measurements over the tropical oceans close to upwelling areas neither at high latitudes in regions of primary productivity. For quantitative analysis, the simulated annual mean CHOCHO vertical columns have been plotted against the SCIAMACHY annual mean observations in 2005 for all grid boxes with SCIAMACHY observations (Fig. 1c). To reduce the variability of the data, the modeled CHOCHO columns were grouped (binned) into values of $0.25 \cdot 10^{14}$ molecules cm^{-2} of SCIAMACHY observational data, independent from the exact location of these observations. Results from both high (S3-H) and low (S3) horizontal resolution simulations have been plotted. It appears that the two simulations behave similarly (no statistical difference) with regard to observations. Both these correlations correspond to linear fits with slopes of 0.43 ± 0.07 and correlation coefficient r of 0.95. Additional comparison of model results with observations, excluding the values over the oceans, indicate better correlation ($r=0.99$) and slope of 0.61 ± 0.07 . This behavior is best explained by

- (a) the existence of primary or secondary tropical sources of CHOCHO over the oceans, neglected or underestimated by the current model;

- (b) a current underestimation of the land sources when only secondary emissions of glyoxal are taken into account by the model.

Figure 1c indicates that at least about 25% of the CHOCHO column is missing in the model when accounting for all data and their variability. Taking into account the global secondary source calculated by TM4-ECPL of 56 Tg y^{-1} this missing CHOCHO source corresponds to about 20 Tg y^{-1} that could be entirely or partially located over the oceans (see further discussion for the existence of primary land sources). Phytoplankton bloom areas could release significant amounts of VOC in the atmosphere (J. Williams, personal communication, 2008). Such emissions are not taken into account in the present study. Note that this discrepancy could be also attributed to an overestimate of glyoxal sinks. Compared to the earlier simulations in Wittrock et al. (2006), in the present study TM4-ECPL is able to reproduce part of the outflow from the continents (Sinreich et al., 2007) and slight enhancement over the tropical oceans and the north Atlantic that are seen by SCIAMACHY. These patterns are under investigation and can not be properly reproduced by TM4-ECPL based on the processes that are actually considered to control CHOCHO levels in the model.

Figure 1d focuses on the low resolution simulations S2, S3 and S4. Taking only the model results over the continents into consideration, the binned data, derived as explained, are plotted in Fig. 1d against the annual mean vertical column of CHOCHO derived from SCIAMACHY. S3 considers all known photochemical sources of CHOCHO. S2 neglects the anthropogenic contribution to the secondary CHOCHO source. Finally, S4 accounts also for potential primary sources of CHOCHO from combustion. Figure 1d suggests that i) TM4-ECPL underestimates the annual mean CHOCHO columns observed by SCIAMACHY in 2005, ii) when accounting for the anthropogenic contribution to the photochemical formation of CHOCHO, TM4-ECPL results compare better with the observations and iii) consideration of primary anthropogenic sources of CHOCHO further improves the general agreement of model results with satellite observations over land.

Figure 1e focuses on 8 hot spot areas around the globe, including China where anthropogenic emissions increase rapidly (see figure caption for the geographic definition of the areas). It appears that i) simulation S3, considering only secondary sources of CHOCHO, agrees with satellite observations over these areas within the 95% confidence level, although generally it underestimates the columns over land (Fig. 1d); ii) simulation S4 overestimates CHOCHO columns over source areas (Fig. 1e), although it seems to perform relatively well (95% confidence level) with regard to the global burden of glyoxal over land (Fig. 1d). Both simulations S3 and S4 underestimate the surface observations as shown in Table 2. Due to the high uncertainties both in potential primary emissions of CHOCHO and in satellite retrievals, these

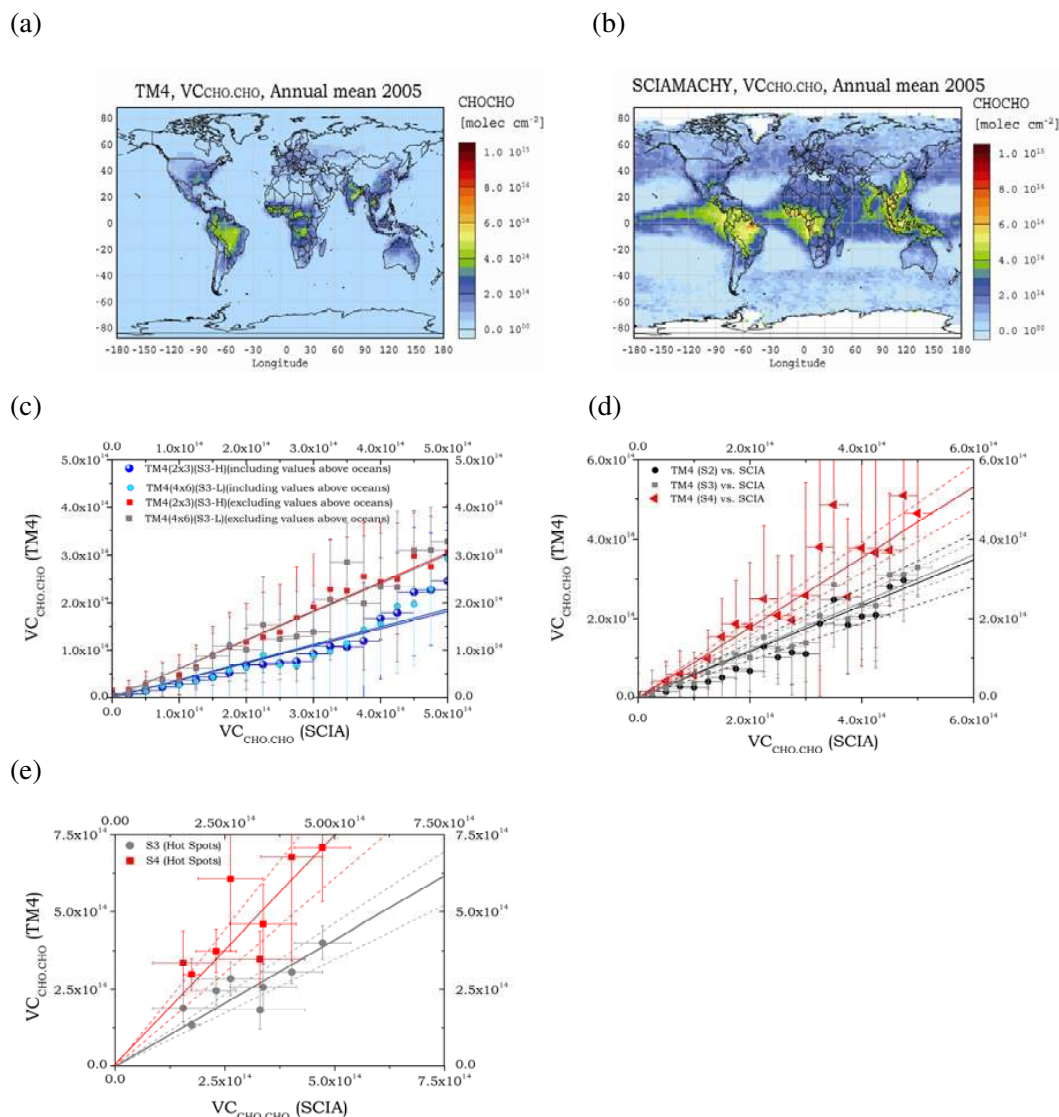


Fig. 1. Global annual mean column distribution of CHOCHO (in $2^\circ \times 3^\circ$ grid) for the year 2005 (in molecules cm^{-2}):

- Simulated by TM4-ECPL, taking into account all glyoxal sources (simulation S3-H).
- Retrieved from the measurements made by the satellite based sensor SCIAMACHY
- Comparison of annual mean glyoxal columns from TM4-ECPL-S3 simulations and SCIAMACHY data product (in units of molecules cm^{-2}). The points show the annual mean simulated columns for the year 2005 binned every 0.25×10^{14} molecules cm^{-2} of the corresponding SCIAMACHY observations, together with their standard deviations. Dark blue circles and light blue are the binned data when both land and oceanic grids are considered for the TM4-ECPL-S3-H and TM4-ECPL-S3 simulations, respectively. Solid red and black squares are the corresponding binned data when neglecting the grid cells over the oceans.
- Comparison of annual mean glyoxal columns from TM4- ECPL simulations and SCIAMACHY data products (in units of molecules cm^{-2}). Binned data over the continents; red triangles are for S4 simulation, solid gray squares for S3 simulation, and solid black circles for S2 simulation. Linear fit regression lines are also plotted with the corresponding color.
- Comparison of annual mean glyoxal columns from the TM4-ECPL simulations S3 (circles) and S4 (squares) with the SCIAMACHY data products (in units of molecules cm^{-2}) over hot spot areas. Linear regression lines given in grey and red (and 95% confidence level interval), respectively, correspond to a slope of 0.81 ± 0.05 ($R^2=0.92$) for S3 and of 1.43 ± 0.14 ($R^2=0.95$) for S4. Hot spot areas are defined as follows: Central Europe (42 N: 54 N; 6 E: 24 E); NE USA (30 N:42 N; 96 W:78 W); Central S America (Amazon) (18 S:6 S; 66 W: 48 W); Central N Africa (2 S:10 N; 12 E:30 E); Central S Africa (18 S:6 S; 12 E:30 E); India (18 N:30 N; 72 E:90 E); China (26 N:38 N; 102 E:120 E); Australia (26 S:14 S; 120 E:138 E).

simulations are not conclusive with regard to the magnitude of the primary CHOCHO source. Overestimate of CHOCHO sink in the model could be responsible for part of the discrepancies between model results and observations.

Figure 2a depicts the distribution of the global annual mean CHOCHO column for the year 2005, computed by the S3 simulation and is compared with that from the SCIAMACHY observations at the same spatial resolution ($4^\circ \times 6^\circ$) shown in Fig. 2c. Figure 2b shows the calculated annual mean column of CHOCHO produced from biogenic VOC oxidation (simulation S1). The majority of the annual mean column of CHOCHO over the tropics, which maximizes at around 5×10^{14} molecules cm^{-2} , is attributed to the oxidation of biogenic VOCs. Annual mean columns smaller than 3×10^{14} molecules cm^{-2} are computed over the Northern Hemisphere mid-latitude continental regions. Note that these biogenically derived CHOCHO columns are slightly smaller than the earlier simulations presented in Wittrock et al. (2006), which did not account for the wet removal of CHOCHO in clouds and used a lower estimate of the photolysis rate of CHOCHO than the present study.

The secondary biomass burning source of CHOCHO from the oxidation of VOCs is taken into account in the simulations (S2 and S3) and is evaluated as the difference between the simulations S2 and S1 that is depicted in Fig. 2e (annual mean column) and Fig. 3i,j (seasonally mean columns). According to our calculations, based on current knowledge of VOCs released by biomass burning, the secondary source of CHOCHO from biomass burning contributes about 3 Tg y^{-1} to the global chemical production of glyoxal and therefore increases its global annual mean burden by about 5%, adding at most 2×10^{14} molecules cm^{-2} to the CHOCHO column over tropical biomass burning areas. As mentioned in Sect. 2.3, primary emissions of CHOCHO from burning in the tropics (and elsewhere) have been considered only in simulation S4. Although these emissions are highly uncertain, they might be of importance for CHOCHO columns over source regions. The contribution of a potential primary source of CHOCHO from combustion, including biomass burning, is depicted in Fig. 2f and is shown to maximize over the tropics. There, primary emissions are evaluated to contribute with up to 8×10^{14} molecules cm^{-2} to CHOCHO annual mean columns (Fig. 2f). Simulations S3 and S4 also calculate significant CHOCHO columns of about 2 to 6×10^{14} molecules cm^{-2} over hot spot regions of anthropogenic activity areas of the USA, Europe, India and China (Fig. 2d and f) that are also detectable from space but are not reproduced in simulations S1 and S2. Note that Fig. 2d depicts the increase in the annual mean column of CHOCHO accounting for CHOCHO production during the oxidation of anthropogenically emitted VOC (difference between simulations S3 and S2). This secondary source of CHOCHO from anthropogenic emissions contributes about 13 Tg y^{-1} to the global chemical production of CHOCHO, i.e. about 20% of the overall chemical production. The CHOCHO global annual mean burden resulting

from the anthropogenic emissions is about 32% of the total; this fraction is larger than the corresponding fraction of the chemical production. This reflects the fact that the secondary anthropogenic source is located mostly in the extra-tropics where the destruction of CHOCHO by photolysis and reaction with OH radical is moderate and thus CHOCHO lifetime is longer than its global mean value.

On the contrary, in S3 the biogenically derived burden of CHOCHO is 63% of the total CHOCHO burden whereas the corresponding chemical production is higher, about 77% of the total. This increased chemical production is compensated by a shorter lifetime of CHOCHO in the tropics. Thus, the computed global lifetime of glyoxal averaged year-around increases from 2.4 h when only biogenic sources are taken into account (S1) and 2.5 h when biomass burning sources are also considered (S2) to 3 h when all secondary sources are taken into account (S3).

Our simulations indicate that the global mean lifetime of CHOCHO critically depends on the location of its sources. In particular, the anthropogenic sources of CHOCHO are more effective in increasing its burden since they are located mostly in the mid latitudes where the photochemical sink of glyoxal is moderate.

4.3 Seasonal variation

The seasonal patterns of the calculated and observed CHOCHO columns have also been compared. Figure 3 depicts the NH winter and NH summer column distributions of CHOCHO as observed by SCIAMACHY (panels 3a and b, respectively) and as calculated by the TM4-ECPL S3 simulation (panels 3c and d, respectively). In the NH, TM4-ECPL simulations show higher CHOCHO columns during summer than during winter in agreement with the satellite observations, reflecting the photochemical origin of CHOCHO and the important contribution of the biogenic VOC oxidation to CHOCHO chemical production (Fig. 3e and f). It is also remarkable that during NH summer the model overestimates the CHOCHO over the Amazon, but not over the African tropical forests. Biomass burning emissions occurring mostly in the tropics have a strong seasonality with significantly different geographical patterns from one season to another. This is reflected in the CHOCHO distribution as depicted in Fig. 3i and j. However, their contribution to the CHOCHO columns is minor compared to that from the biogenic VOC oxidation (Fig. 3e and f). The most likely explanation of the model overestimate of CHOCHO columns is related to the biogenic VOC emission inventory used.

Biogenic VOC emissions are enhanced under warm and sunny conditions (Guenther et al., 2006); between 30° N and 60° N are about 50 times higher during summer than during winter. On the contrary, the anthropogenic VOC emissions present a much weaker seasonality. In our model simulations this seasonality is neglected, because both the EDGAR and POET emissions database do not provide information on

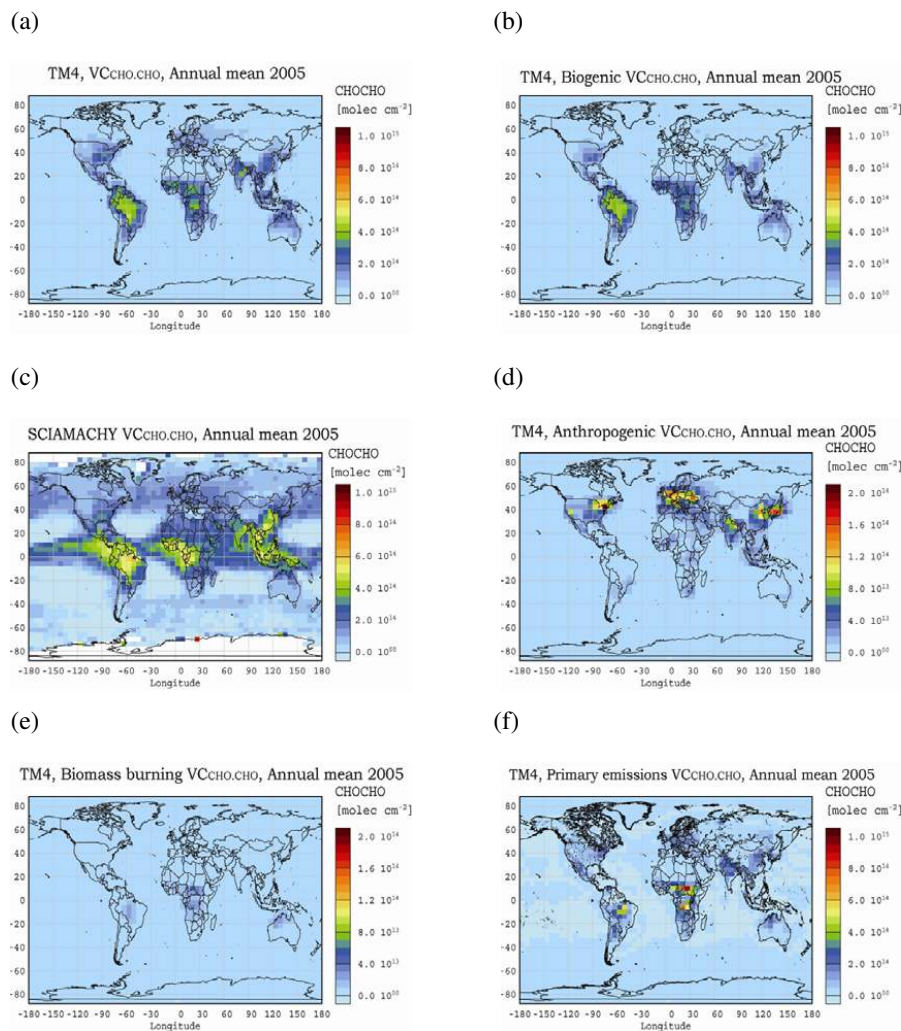


Fig. 2. Global annual mean column distribution of CHOCHO (in $4^\circ \times 6^\circ$ grid) for the year 2005 (in molecules cm^{-2}):

- (a) Simulated by TM4-ECPL taking into account all secondary glyoxal sources (simulation S3).
- (b) Simulated by TM4-ECPL taking into account only the CHOCHO source from biogenic VOC oxidation.
- (c) Observed by the satellite based sensor SCIAMACHY (reduced spatial resolution)
- (d) Simulated by TM4-ECPL to be produced by the anthropogenic VOC oxidation
- (e) Simulated by TM4-ECPL to be produced by the biomass burning VOC oxidation
- (f) Simulated by TM4-ECPL to result from primary emissions from biomass burning and other combustion sources.

the seasonal variability of the anthropogenic VOC emissions. The calculated hydroxyl radical concentration, the main tropospheric oxidant responsible for CHOCHO formation, exhibits a strong seasonality, having a summer-to-winter ratio that varies near the surface in the northern troposphere mid-latitudes from about 2 to more than 20, as presented in Fig. 4. The strong seasonality in oxidant levels and biogenic emissions leads to about 25% higher global production of CHOCHO during the NH summer than during the NH winter (Fig. 3g and h). In parallel, the losses of CHOCHO are

also about 25% higher during summer as a result of increased losses of CHOCHO by photodissociation (20%), by reaction with the OH radical (40%) and by deposition (25%). The overall result is an almost 10% enhancement of the CHOCHO column during NH summer (global burden 0.019 Tg) compared to NH winter (global burden 0.017 Tg). The consideration of potential primary sources of CHOCHO (simulation S4) is also introducing significant seasonality since biomass burning emissions maximize during the dry season. The estimated seasonal contribution of this primary source

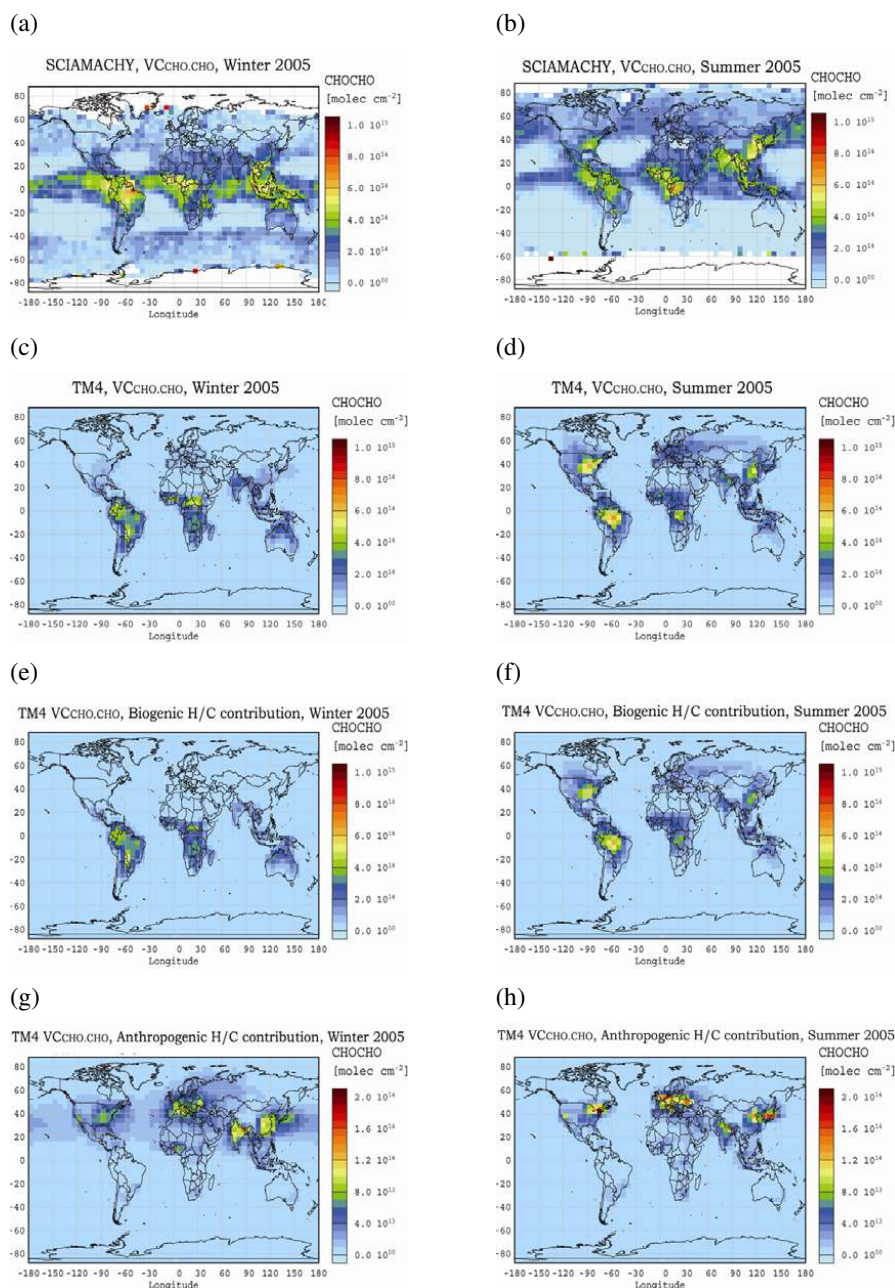


Fig. 3. NH winter (a, c, e, g, i, k) and NH summer (b, d, f, h, j, l) mean columns of glyoxal as retrieved from SCIAMACHY observations (a, b) and as computed by TM4-ECPL taking into account formation of glyoxal from VOC emitted from (c, d) all sources; (e, f) only biogenic sources; (g, h) only anthropogenic sources and (i, j) only biomass burning, for the year 2005. (k, l) computed CHOCHO columns derived from biomass burning and other combustion primary sources. Columns are given in 10^{15} molecules cm^{-2} . Note the different color scale in figures g to j.

to CHOCHO column is shown in Fig. 3k and l. Finally, in the present study, a potential aerosol sink of CHOCHO that could be of relevance for atmospheric conditions is not taken into account, because of our limited current knowledge about this process.

4.4 Ratios of trace gases columns

As a result of the strong anthropogenic signal in the CHOCHO column, it is expected that synergistic use of CHOCHO and HCHO observations from space provides a powerful tool to evaluate the impact of VOC emissions on tropospheric

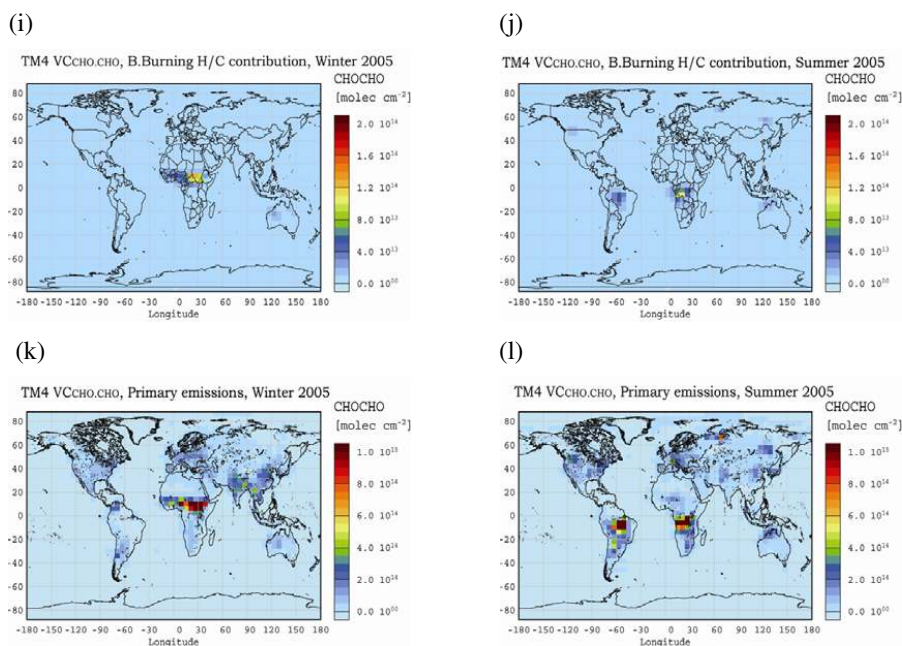


Fig. 3. Continued.

chemistry, as a function of source region and type. This proposition has been investigated by examining the computed ratios of CHOCHO to HCHO over the tropics and over the hot-spot areas in the Northern Hemisphere. The satellite observations of CHOCHO and HCHO molecules were used to compute the respective ratio above the 30 most populated areas of the world (<http://www.infoplease.com/ipa/A0884418.html>). The mean CHOCHO/HCHO ratio above these regions is 0.037 ± 0.014 . This mean ratio is in good agreement with the value of 0.025 observed in Mexico City based on the data provided by Garcia et al. (2006), and taking into account the diurnal profile of these carbonyls to match the satellite overpass time. The same analysis performed above biogenic sources gave an enhanced average value equal to 0.050 ± 0.025 . This latter number is in good agreement with the range of values 0.04–0.06 reported by Munger et al. (1995) and Spaulding et al. (2003). These values are contrasted with those computed by the TM4-ECPL model (Fig. 5a): the model calculated ratios, derived from the 10–11 a.m. local time simulations, are in reasonable agreement with the satellite data (not shown) over the selected regions with intense anthropogenic emissions, namely Europe, China, India and the United States. Figure 5b illustrates the same ratio when the anthropogenically produced CHOCHO is ignored (simulation S2). As expected, the major impact of this photochemical source of CHOCHO is seen above the Northern Hemisphere urban areas.

The differences in the CHOCHO to HCHO ratio between simulations S3 and S2 that is attributed to the photochemical source of CHOCHO from human activities is shown in

Fig. 5c in which the anthropogenically influenced regions are clearly identified.

4.5 CHOCHO annual global budget

According to the TM4-ECPL simulations, CHOCHO global annual chemical production totals $56 \text{ Tg CHOCHO } \text{y}^{-1}$. Approximately 70% results from the oxidation of biogenics, isoprene and terpenes, among which the predominant portion is formed via formation of glycolaldehyde and hydroxyacetone and subsequent degradation. To a smaller extent CHOCHO is formed from AVOCs, i.e. 17% from acetylene, 11% from aromatics, and 2% from ethene and propene. According to the TM4-ECPL model simulations, the contribution of anthropogenic VOCs oxidation to the CHOCHO column is limited to 3–20% over the tropics and maximizes over urban areas and downwind in the Northern Hemisphere, reaching values of 20–70%. However, the CHOCHO column is relatively low (~ 2 to $\sim 4 \times 10^{14}$ molecules cm^{-2}) in the anthropogenic influenced regions. This is consistent with findings in Mexico City, where aromatics contribute some 70–80% to the CHOCHO production rate. A direct comparison of the relative contribution of individual VOC sources and CHOCHO sinks is possible for Mexico City (data from Table 1 of Volkamer et al., 2007) and the Pearl River Delta (Volkamer et al., 2006b), and shows good agreement with the model results of this study. Consideration of primary CHOCHO sources would further increase by about 20% the anthropogenic and by about 160% the biomass burning annual CHOCHO sources. TM4-ECPL also evaluates that the glyoxal secondary production from biogenic and biomass

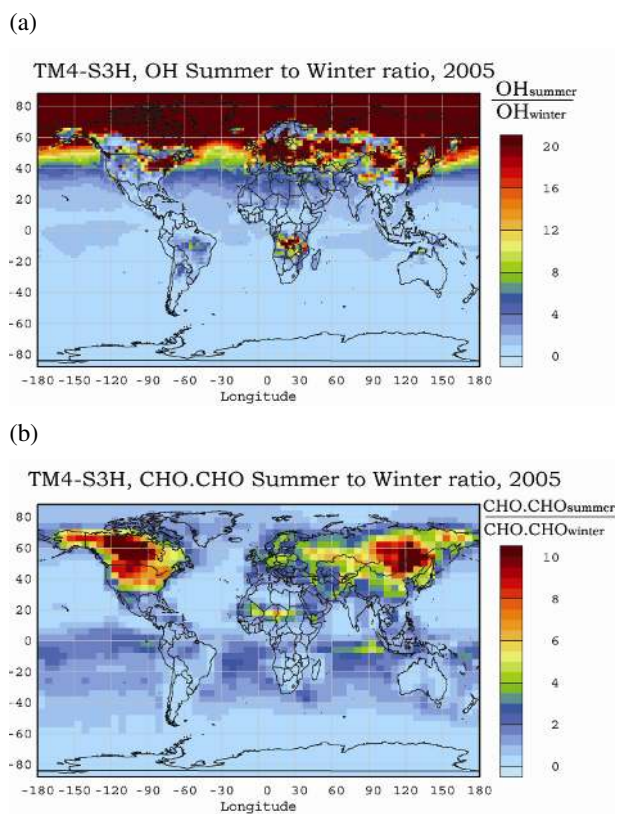


Fig. 4. NH Summer to NH winter ratios of (a) computed OH radical, (b) of computed glyoxal column (simulation S3-H).

burning VOC oxidation has been significantly enhanced (almost doubled) due to the changes in oxidants levels induced from anthropogenic activities.

CHOCHO is destroyed by photolysis (63%), and OH radical reactions (23%), but it is also removed from the atmosphere through wet deposition (8%) and dry deposition (6%). As a result, for CHOCHO the global annual mean burden in the model domain equals 0.02 Tg (equal to the global burden seen by SCIAMACHY over land in the year 2005) and the lifetime is around 3 h.

It is also remarkable that according to our model simulations, on an annual basis about 5 Tg of CHOCHO are removed from the atmosphere via wet deposition. The robustness of this result is investigated by simulation S5 that used a 2 orders of magnitude lower K_H for CHOCHO. In that simulation, both the lifetime and the global burden of CHOCHO increase by about 2% as a result of a reduction in its wet deposition by about 8%. Note that this loss of CHOCHO in clouds has the potential to form secondary organic aerosol as the result of cloud processing of glyoxal, and has to be considered as an indication of the order of magnitude for glyoxal contribution to SOA formation via this procedure. Recently, Fu et al. (2008) have evaluated this source of SOA from glyoxal at 2.6 Tg y^{-1} . Evidence for glyoxal related SOA forma-

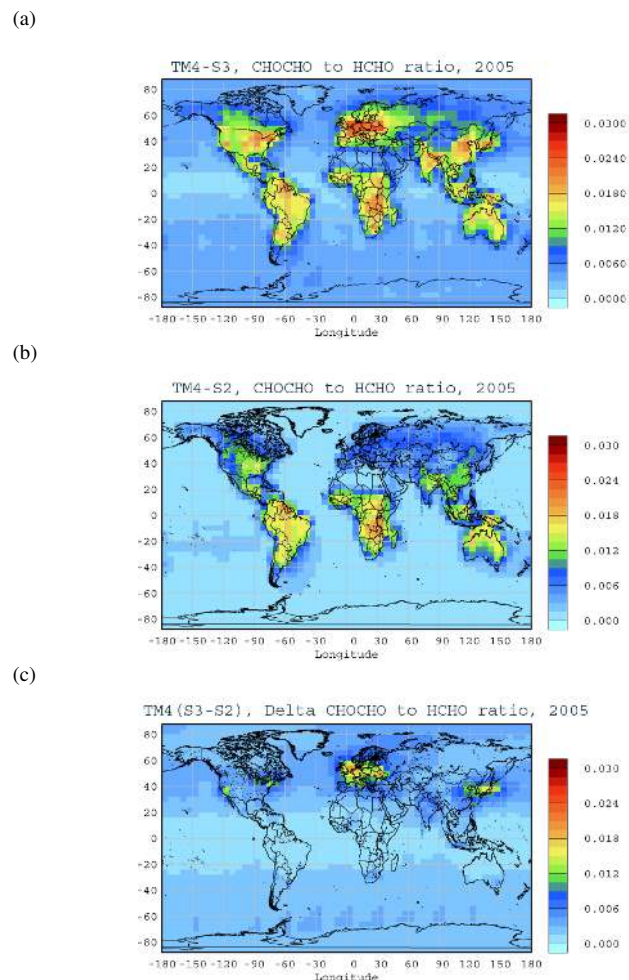


Fig. 5. Annual mean ratios of CHOCHO to HCHO as simulated by TM4-ECPL (a): simulation S3 and (b): simulation S2. (c) Difference in this ratio is attributed to the anthropogenic contribution to the CHOCHO column.

tion in the absence of clouds as recently indicated by Volkamer et al. (2007) may however add further SOA. This topic requires further investigation and refinement.

5 Conclusions

The global 3-dimensional chemistry/transport model TM4-ECPL has been adapted to simulate the temporal and spatial distribution of CHOCHO columns in the global troposphere. This study has focused on the anthropogenic contribution to the CHOCHO column amounts and their seasonality. Aromatics and other hydrocarbons of anthropogenic origin play an important role in determining CHOCHO column abundances. Wittrock et al. (2006) showed significant amounts of CHOCHO above highly populated regions retrieved from the measurements by the SCIAMACHY sensor aboard ENVISAT. The enhanced CHOCHO columns

above these regions are confirmed by ground-based satellite validation efforts in Mexico City, and the Pearl River Delta, China (Volkamer et al., 2006b). The global annual chemical production of CHOCHO has been calculated by the TM4-ECPL model to be 56 Tg CHOCHO y^{-1} . Compounds of anthropogenic origin account for about 30% of the total chemical production of CHOCHO; acetylene producing about 17% and aromatic hydrocarbons (toluene, xylene and benzene) about 11%. According to TM4-ECPL model calculations, the contribution of anthropogenic VOC to the CHOCHO column is in the range of 3–20% over the tropics and maximizes over urban-influenced areas in the Northern Hemisphere where it reaches 70%. Primary emissions of CHOCHO could increase the anthropogenic contribution to the global annual CHOCHO source by about 5%. The improvements in the model chemistry of CHOCHO compared to the earlier study by Wittrock et al. (2006) resulted in better agreement between the model results and the glyoxal observations in the mid latitudes. However, comparison of model results that take into account only the secondary source of CHOCHO with satellite observations indicates a missing CHOCHO source of about 20 Tg y^{-1} or an overestimate of its sinks by the model. In particular, the model does not capture the enhancement of CHOCHO columns over the tropical ocean seen by SCIAMACHY. This points to the existence of primary and/or secondary tropical and/or oceanic sources of CHOCHO, currently neglected or underestimated by the model.

Our model simulations evaluate that 5 Tg CHOCHO y^{-1} are removed by precipitating clouds. This amount indicates the order of magnitude of a potential CHOCHO contribution to the SOA formation via multiphase chemistry in clouds. This estimate deserves careful and further refinement. The current limited description of the role of primary production in oceans, the release of particles and organic compounds from oceans, the physics and chemistry of clouds and possibly aerosols introduce significant uncertainties in the modeled CHOCHO and require further study.

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