GLOBAL OBSERVATIONS OF GLYOXAL (CHOCHO) FROM SPACE

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ESF-INTROP

ABSTRACT

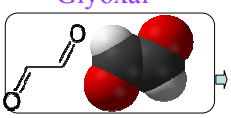
The fate of Volatile Organic Compounds (**VOC**) emissions is of great scientific interest because VOC species are involved to photochemical smog, to ozone changes and to secondary organic aerosols (**SOA**) formation due to the low volatility of the oxidized products. An important molecule of the VOCs is the glyoxal (**CHOCHO**). Glyoxal is the smallest dicarbonyl which is mainly formed via the oxidation of VOCs by the OH radicals. Since no direct sources are known for this species it can serve as a tracer of the photochemical smog produced by the fast chemistry linked to volatile organic compounds oxidation.

Global satellite composite images of CHOCHO retrieved from the SCIAMACHY instrument, on board of the ENVISAT satellite. CHOCHO is derived by the differential optical absorption technique (DOAS) which is applied to scattered light spectra in the VIS-blue spectral range (**436.0–457.0 nm**). Monthly and annual means of glyoxal were calculated for four years (**2003 to 2007**). Enhanced values of glyoxal were found above Central Africa, South America (mainly Brazil), India, China and Indonesia as well as some major cities of Europe and the United States. These values were associated **a) with biomass burning b) with anthropogenic activities** and **c) with biogenic emissions** revealing that the global distribution of CHOCHO is affected by both anthropogenic and biogenic emissions.

The satellite vertical columns are compared with the simulations of a **3d global atmospheric chemistry transport model (TM4)** driven by ECWMF meteorology. Overall, measurements and model results agree reasonably well.. However, differences over some specific regions point to gaps in our current understanding of the sources and/or the relevant chemistry of glyoxal in the atmosphere. Further work is needed to come to quantitative agreement between measurement and model results.

INTRODUCTION

Glyoxal



CHOCHO is formed by the oxidation of NMHC. Contrary to HCHO no direct sources are expected. This makes CHOCHO a better indicator of the VOC oxidation.

SOURCES

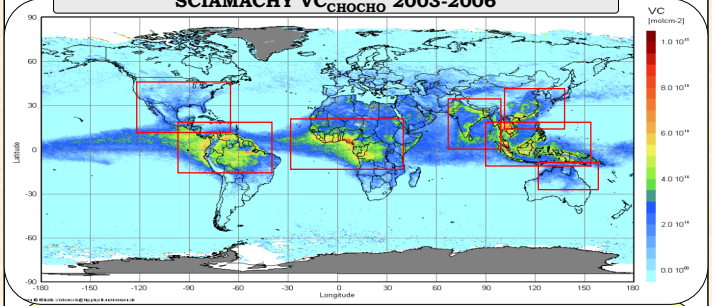
SINKS

The main known **sinks** of CHOCHO are: a) the reaction with the **OH radicals** and the b) **photolysis** leading to an estimated lifetime 1.5h

Results: GLOBAL VIEW OF CHOCHO

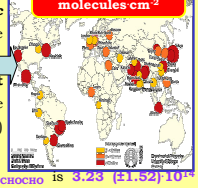
Glyoxal vertical columns have been retrieved for the period **1.1.2003 – 31.12.2006**. The figure below depicts the global multi-annual composite of CHOCHO. Several areas inside the ***red squares*** appear to have enhanced vertical CHOCHO column values pointing to the presence of photochemical hot spots. Some of these areas are located in **South America, Africa, East USA**, the developing **Asian cities**, **India, Indonesia** and to a lesser extent in Europe.

SCIAMACHY VC_{CHOCHO} 2003-2006

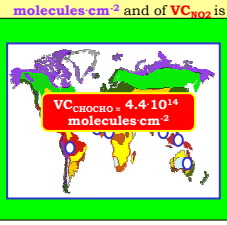


At a first glance it was found that the highest glyoxal values are observed near the various source regions (***anthropogenic, biogenic and biomass burning***) indicative of the short atmospheric lifetime of CHOCHO.

In order to provide a first estimation of the **anthropogenic impact** on the glyoxal levels, the mean annual value of CHOCHO above the 36 most populated cities and megacities of the world (right picture) has been calculated.

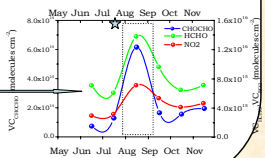


For the 3 years period, fro these areas the mean value of VC_{CHOCHO} is **3.23 (±1.52)·10^15 molecules·cm^-2** and of VC_{NO2} is **6.26 (±2.57)·10^15 molecules·cm^-2**.

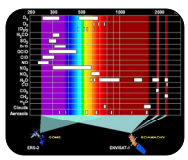


Similar evaluations performed for some spots of enhanced **biogenic activity** (left picture – yellow spots) show that the mean estimated annual VC_{CHOCHO} value, **4.41 (±1.22)·10^14 molecules·cm^-2**, is somehow greater than the anthropogenically influenced areas. The respective VC_{NO2} levels **(~6.10^14 molecules·cm^-2)** are one order of magnitude lower than the respective ones found over urban areas.

Another important factor linked to high glyoxal vertical column values is **biomass burning emissions**. For example, in August and September 2003, the monthly mean VC_{CHOCHO} over Portugal is about **4 times** above the normal levels due to intensive fires (as observed by the Along Track Scanning Radiometer). Similar increase has been observed for several biomass burning events .



INSTRUMENTATION & EXPERIMENT

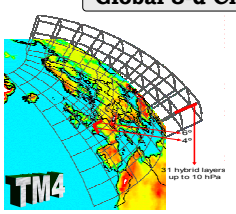


SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY) is an imaging spectrometer whose primary mission objectives is the global measurement of trace gases in the troposphere and in the stratosphere. The solar radiation transmitted, backscattered and reflected from the atmosphere is recorded at relatively high resolution **(0.2 nm to 1.5 nm)** over the **range 240 nm to 1700 nm**, and in selected regions between 2.0 μm and 2.4 μm. Sciamachy has a **global coverage of 6 days** with a **spatial resolution of 60kmx30km.**

The vertical columns (VC) of glyoxal are calculated with the Differential Optical Absorption Spectroscopy (DOAS) and subsequently applying the air mass factor correction (*AMF*, calculated by the radiative transfer model *SCIATRAN*) to the slant columns (SC). The latter is the integrated amount of absorber averaged over all light paths. CHOCHO was retrieved at the blue spectral range at 436.0–457.0 nm. The main steps of the retrieval technique are listed below:

- The logarithms of the earthshine spectra and the solar irradiance are normalised to produce an absorption spectrum.
- Broadband features due to Mie and Rayleigh scattering are removed via the fitting of a low order polynomial.
- Ring spectrum is fitted to correct the rotational and vibrational Raman Scattering
- Other absorbers (in addition to the species of interest) interfering at the above mentioned wavelengths are fitted. In case CHOCHO these were the O_3, NO_2, H_2O and O_4. The SC are calculated by applying the Lambert-Beer law
- The final step involves the conversion of the SC to VC via the AMF

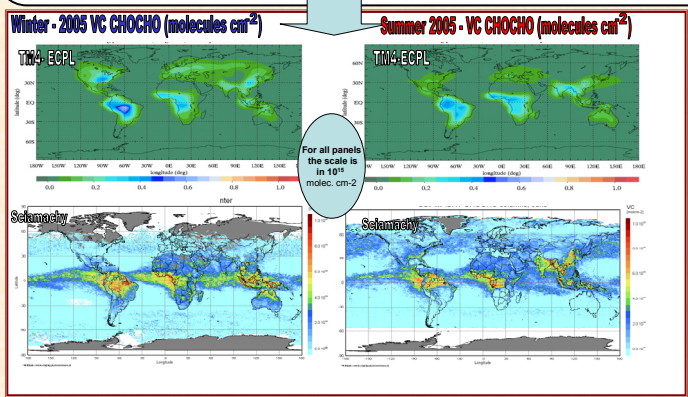
Global 3-d Chemistry-Transport Model (TM4) & results



TM4 model is able to describe both ***gas phase chemistry and all major primary and secondary aerosol components, including secondary organic aerosol*** (SOA). It considers the sulphur and ammonia chemistry and the oxidation of C_1-C_5 Volatile Organic Compounds including isoprene, as well as a highly simplified terpenes and aromatic chemistry. ***It explicitly considers glyoxal and carboxylic acids formation in the troposphere.***

Other TM4 parameterisations:

- TM4 has 31 vertical hybrid levels from the surface to 10 hPa and is able to run in two horizontal resolution analysis : One high (2° lat. x 3° lon) and one low (4° lat. x 6° lon).
- Advection. *(Russell and Lerner (1981) J. Appl. Met.* **20**, 1483)
- Convection. *(Tiedke (1989) Mon. Weather Rev.* **117**, 1641)
- Turbulent mixing. *(Louis (1991) Boundary Layer Met.* **17**, 187)
- Meteorology input from ECMWF re-analysis project data-archive: 6 hourly data of geopotential height, temperature, specific humidity and horizontal winds. (http://www.ecmwf.int/data/era.html)
- Emissions from *GEIA (Guenther et al., 1995)* and *EDGARv2.0 (Olivier et al., 1996)* inventories have been adopted.

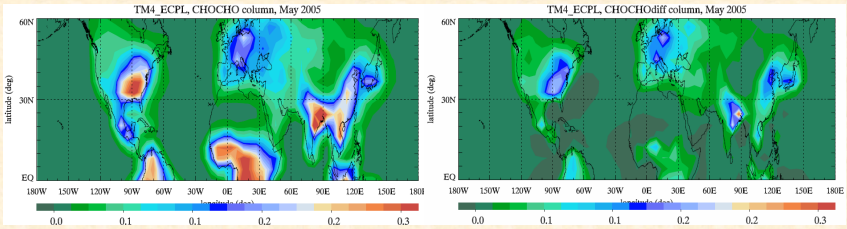


There is a reasonable agreement between the simulated and retrieved glyoxal columns. However, some underestimate by the model is detected mainly over the tropical marine locations. This will be improved in future simulations by better representation of the marine emissions of organic compounds and of multiphase chemistry.

TM4-ECPL model results allow the evaluation of the impact of anthropogenic emissions on glyoxal columns in the northern hemisphere: Simulations considering all sources and neglecting the formation of glyoxal from anthropogenic hydrocarbons.

Glyoxal columns – all sources (in 10^{15} molec cm^{-2})

Increase in glyoxal column due to anthropogenic acetylene and aromatics (in 10^{15} molec cm^{-2})



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