Long-term measurements of glyoxal (CHOCHO) and formaldehyde (HCHO) from space

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ABSTRACT

It is well known that **VOC** are released into the atmosphere by both anthropogenic and natural sources (e.g. *fossil fuel combustion, biomass burning and biogenic emissions*). Nevertheless the discrimination of these sources is difficult due to the overall great uncertainty of their emissions. In order to better characterize these sources, tracers of the oxidation of the VOCs such as **HCHO** and **CHOCHO** are used as proxies. **Formaldehyde**, the smallest aldehyde in the atmosphere is primarily formed through the oxidation of VOC by OH but is also directly emitted. **Glyoxal**, the smallest dicarbonyl, is a mutagenic product formed mainly under the chemical reactions of VOC with OH radicals.

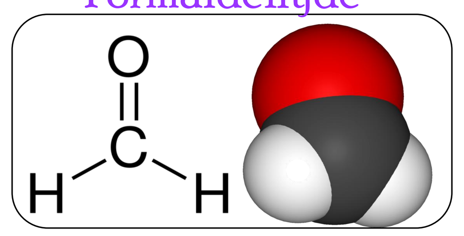
This work presents for the first time concurrent results of both species measured on a global scale for a period of **4 years** covering the period of **2003-2006**. The results were obtained by applying the differential optical absorption technique (DOAS) to spectra measured by the satellite instrument **SCIAMACHY**. HCHO has been analyzed in the spectral region of **334.3–348.5 nm** to avoid any correlation with an instrument grating polarisation structure around 360 nm. CHOCHO was retrieved in the blue spectral range at **436.0–457.0 nm**.

The annual and seasonal variation of these species is examined above some photochemical hot spots induced by anthropogenic and biogenic activities. Some of these areas of interest are the Central Africa, South America (mainly Brazil), India, China and Indonesia as well as some major cities of Europe and the United States. During the period 2003-2006 and on an annual basis the vertical column (VC) values of formaldehyde ranged from **DL (4.10^{15}) – $2.5{\cdot}10^{16}$ molecules.cm^{-2}** while the respective glyoxal values ranged from **DL ($2{\cdot}10^{14}$) – $2{\cdot}0{\cdot}10^{15}$ molecules{\cdot}cm^{-2}**.

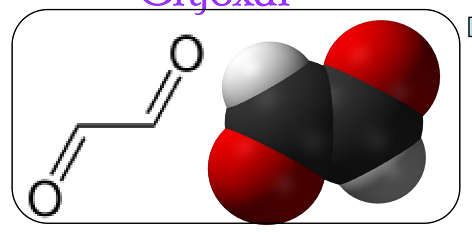
INTRODUCTION

Current knowledge!

Formaldehyde



Glyoxal



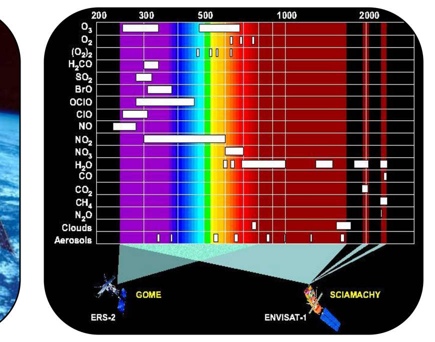
SOURCES

- **HCHO** is mainly produced by the oxidation of methane **(CH_4)** and Non-Methane hydrocarbons **(NMHC).**
- It is also (to a lesser extend) **primarily emitted** by anthropogenic and biogenic sources.
- **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.

SINKS

The main known **sinks** of HCHO and CHOCHO are: a) the reaction with the **OH radicals** and the b) **photolysis** leading to an estimated lifetime of 3.5h and 1.5h respectively.

INSTRUMENTATION & EXPERIMENT



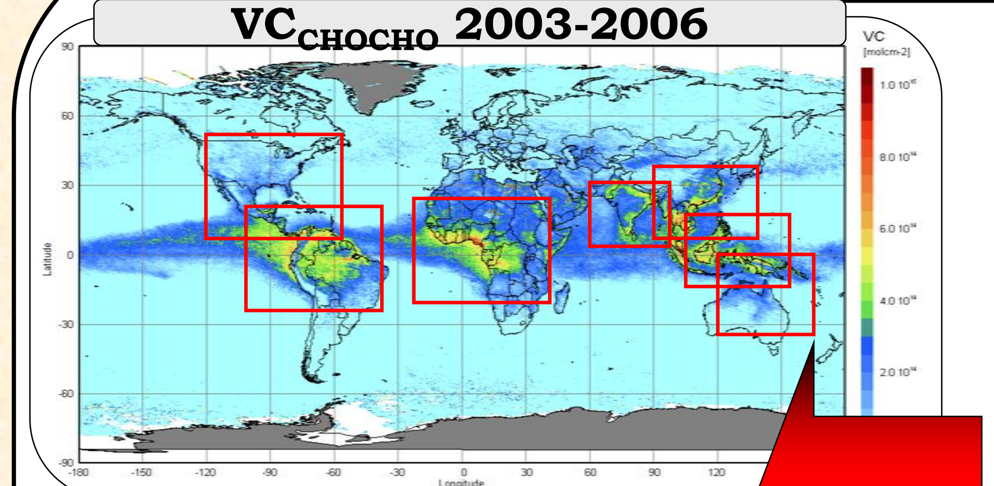
SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY) is an imaging spectrometer whose primary mission objective are global measurements of trace gases in the troposphere and in the stratosphere. The solar radiation transmitted, backscattered and reflected from the atmosphere 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 HCHO and 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. HCHO has been analyzed in the spectral region of 334.3–348.5 nm to avoid any correlation with an instrument grating polarisation structure around 360 nm. CHOCHO was retrieved at the blue spectral range at 436.0–457.0 nm. The main steps of the retrieval technique are listed below:

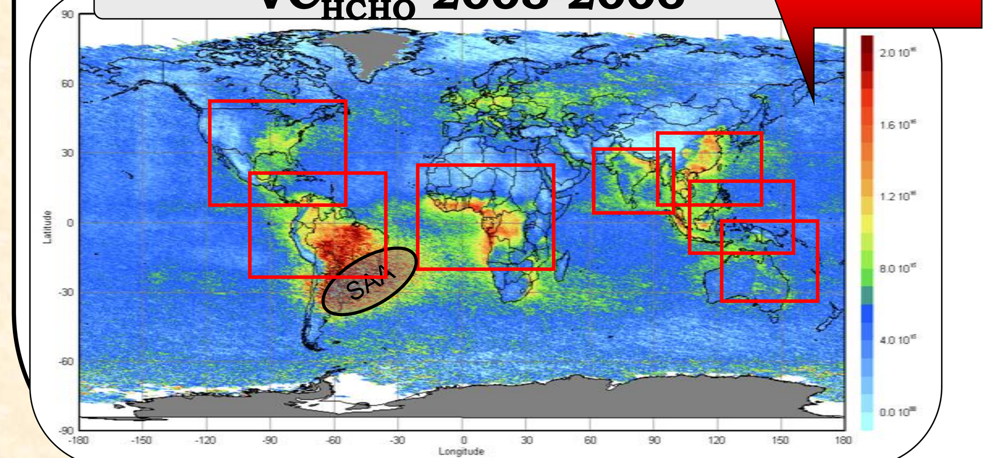
- The logarithms of the earthshine spectra and the solar irradiance are normalised to produce an absorption spectrum.
- Broadband features due to Mie and Rayleigh scattering are removed via the fitting of a low order polynomial.
- Ring spectrum is fitted to correct the rotational and vibrational Raman Scattering
- Other absorbers (in addition to the species of interest) interfering at the above mentioned wavelengths are fitted. In case of HCHO and CHOCHO these were the BrO, 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

RESULTS - ANNUAL VARIATION

VC_{CHOCHO} 2003-2006

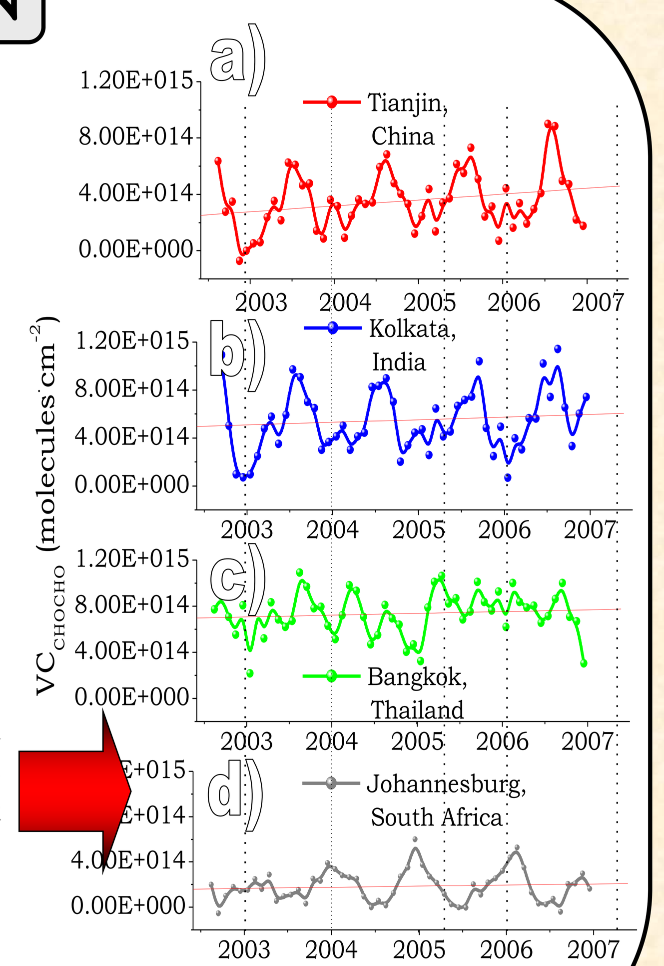


VC_{HCHO} 2003-2006

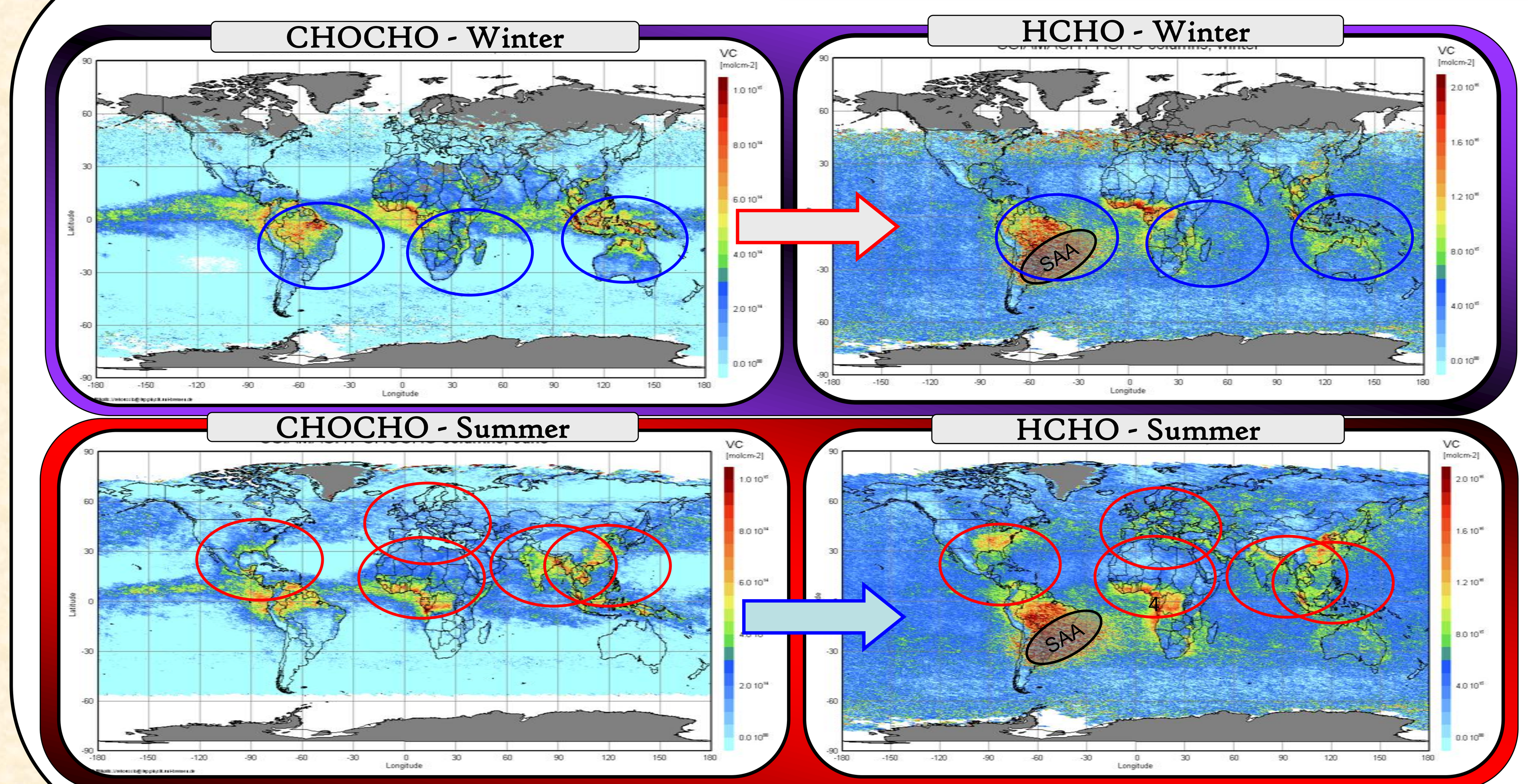


Glyoxal and formaldehyde were calculated on an annual basis for the period **1.8.2002 – 31.12.2006**. The figures to the left depicts the global multi-annual composite for the two species. Certain areas appear to have concurrent enhanced vertical column values for both CHOCHO and HCHO pointing to the presence of photochemical hot spots. Some of these areas are found at **South America, Africa, East USA**, the developing **Asian cities, India** and to a lesser extent Europe. At a first glance it was found that the highest glyoxal values were observed near the various source regions (***anthropogenic, biogenic and biomass burning***). This could be associated with the short lifetime of the CHOCHO.

The graph to the right presents the annual variation of glyoxal above four indicative areas where glyoxal a) had increased during the last years **(Tianjin)**, b) maintained its levels **(Kolkata)**, did not have a seasonal variation **(Bangkok)** and d) had winter maxima (Southern Hemisphere, **Johannesburg).**

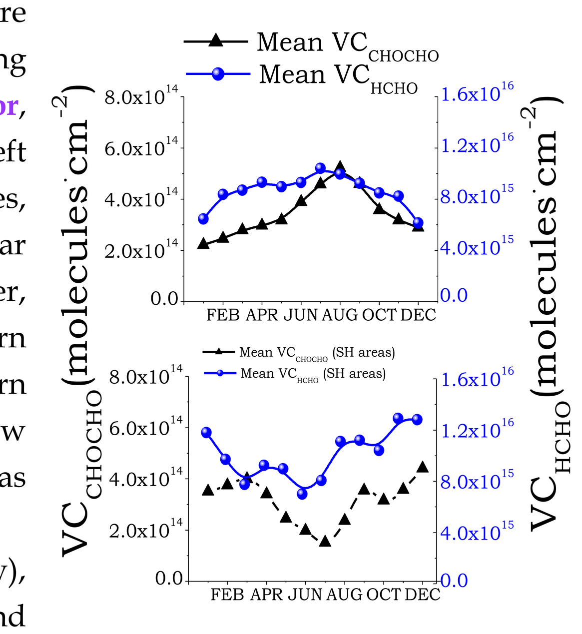


SEASONAL VARIATION



The retrieved SCIAMACHY data of CHOCHO and HCHO, for the period 2003 – 2006 were also analyzed on a seasonal basis by calculating the average value of winter months (blue color, left figure) and summer months (red color, left figure). It was found that in most of the cases, both glyoxal and formaldehyde show similar seasonal behavior. For instance, during winter, the observed maxima are found in the southern hemisphere, while during summer the northern hemisphere dominates. This enables us to draw the conclusion that both species have short as well comparable lifetimes.

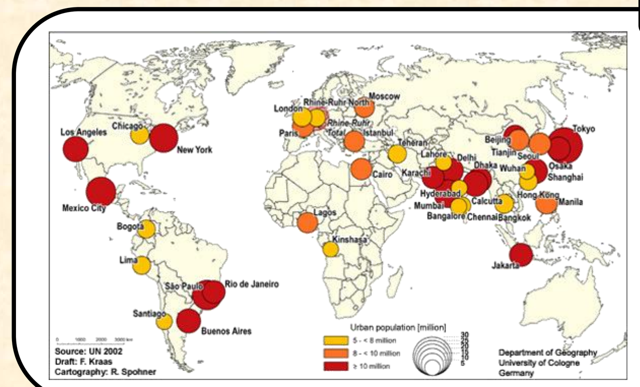
For the areas chosen (see the analysis below), the mean monthly value of CHOCHO and HCHO was calculated (right graph). It can be seen that during **warm** conditions both species maximize. This is mainly due to the **enhanced OH** that controls the VOC oxidation and produces the HCHO and the CHOCHO.



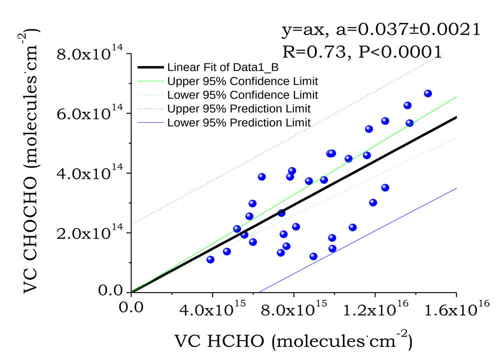
VC-CHOCHO-NH:	$3.46{\cdot}10^{14}$	$9.32{\cdot}10^{13}$
VC-CHOCHO-SH:	$3.14{\cdot}10^{14}$	$8.71{\cdot}10^{13}$
VC-HCHO-NH:	$8.63{\cdot}10^{15}$	$1.26{\cdot}10^{15}$
VC-HCHO-SH:	$1.01{\cdot}10^{16}$	$1.95{\cdot}10^{15}$

All values are in molecules·cm^{-2}

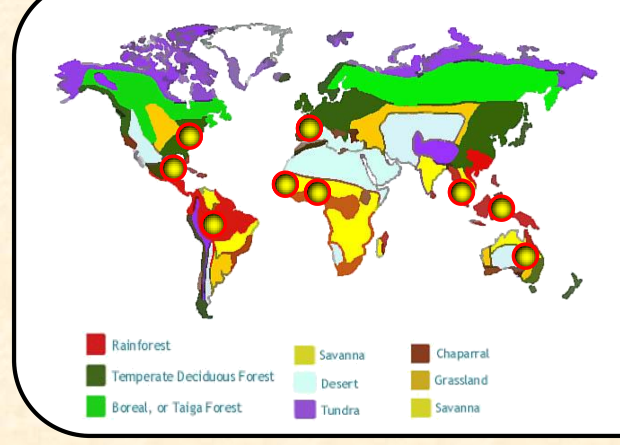
Anthropogenic sources



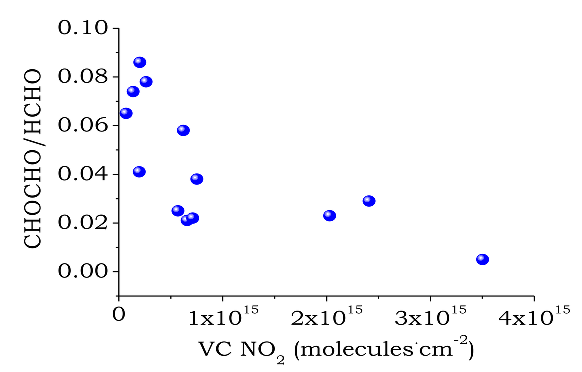
To evaluate the impact of the anthropogenic activities on glyoxal production the mean annual values above 36 large cities and megacities (left picture) were computed. The mean annual value of **VC_{CHOCHO}** was **(3.23 1.52)·10^{14} molecules·cm^{-2}** while the average value of **VC_{HCHO}** was equal to **(8.61 3.95)·10^{15} molecules·cm^{-2}**. Annual **VC_{NO2}** was **(6.26 2.57)·10^{15} molecules·cm^{-2}**. On average CHOCHO was about **3.5%** of the HCHO for the studied cities (right graph).



Biogenic sources

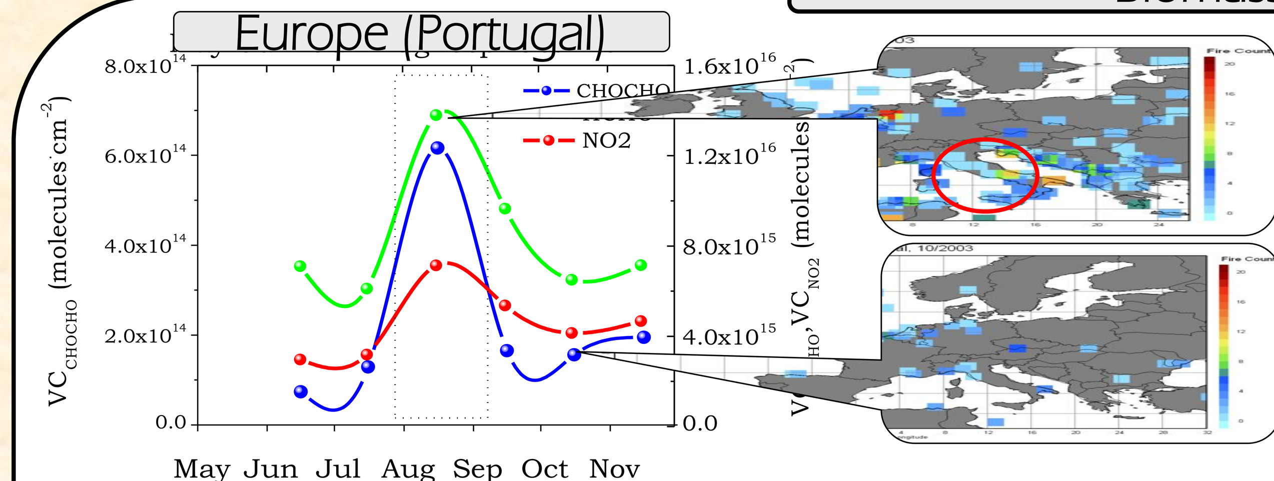


Glyoxal and formaldehyde were averaged on a monthly basis above various biogenic sources as depicted to the map on the left with yellow spots. The mean value of the vertical column of CHOCHO was somewhat higher in comparison to anthropogenic sources and equal to **(4.41 1.22)·10^{14} molecules·cm^{-2}**. The ratio $VC_{CHOCHO}/_{HCHO}$ was about **5%.** It should be noted that the mean annual VC_{NO2} levels **(~6.10^{14} molecules·cm^{-2})** were one order of magnitude lower than the respective ones found for the cities. Nevertheless these levels seem to affect drastically the ratio VC_{CHOCHO}/VC_{HCHO} (right figure) .



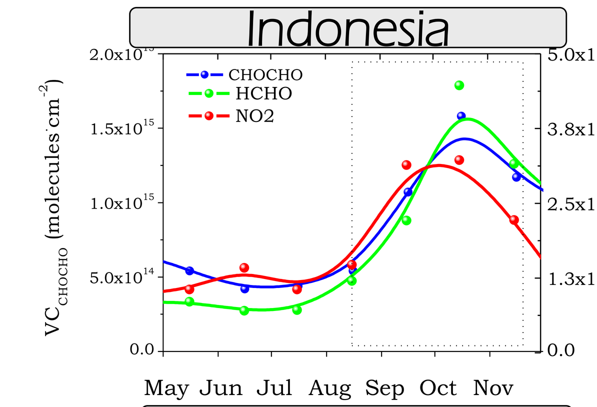
Biomass burning events

Europe (Portugal)

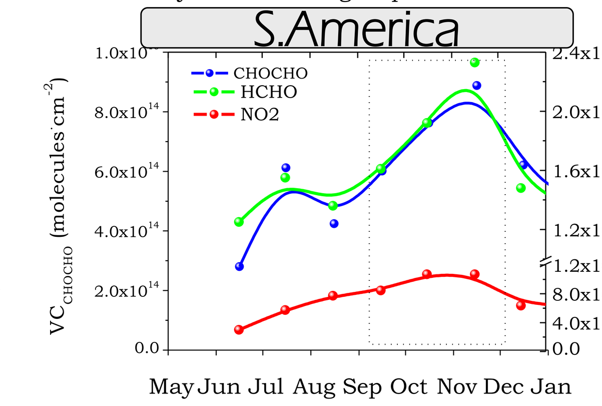


The changes to CHOCHO and HCHO as well to NO_2 vertical column levels were examined during three periods of intensive fires as observed by the analysis of the **ATSR** database (Along Track Scanning Radiometer). In 2003, in August and in September Portugal's glyoxal VC raised about **4 times** above the normal levels due to biomass burning events (see graph above). The same increase (**3-4 times**) was observed over Indonesia (graph in the upper right corner) and South America (lower right graph). During those fire events HCHO has similarly increased and the respective CHOCHO/HCHO was found to be constant and equal to **0.04**.

Indonesia



S.America



Conclusions

- Four years of concurrent CHOCHO and HCHO measurements from space.
- Similar annual and seasonal behavior of CHOCHO and HCHO at specific areas.
- Higher levels of CHOCHO above areas with biogenic, anthropogenic sources as well as biomass burning areas.
- CHOCHO was about 3.5% of HCHO (annual average) above cities.
- CHOCHO was about 5.0% of HCHO (annual average) above biogenic sources.
- CHOCHO increases about 3-4 times (monthly averages) above biomass burning places.

Aknowledgments

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