# Formaldehyde Columns from GOME: Improved Retrievals and their Comparison with the IMAGES Model.

ACCENT task: Satellite observations.
I. De Smedt, M. Van Roozendael and J.-F. Müller. (e-mail: isad@aeronomie.be)
BIRA-IASB, Avenue Circulaire 3, B-1180 Brussels, Belgium.

## *Abstract*

Formaldehyde (HCHO) is the most common carbonyl by-product in the degradation of atmospheric VOCs. Therefore, the opportunity provided by the GOME instrument to quantify the abundance of atmospheric formaldehyde is expected to provide new constraints on the budget of CO as well as on the emissions of non-methane VOCs (NMVOCs), which play a key role in the budget of tropospheric ozone and the hydroxyl radical, the main cleansing agent of the troposphere. In this study, global distributions of formaldehyde columns are retrieved from GOME for the year 1997 using the differential optical absorption spectroscopy technique (DOAS). Analysis settings are carefully optimized for this trace species, and altitude-resolved air mass factors (AMFs) are consistently applied to different sets of formaldehyde profiles derived from the global tropospheric Chemistry Transport Model IMAGES. The synergy between GOME retrievals and model simulations is used to investigate the sensitivity of the global HCHO column distributions to change in anthropogenic, biogenic and pyrogenic NMVOC emissions as well as on potentially uncertain parameters in their degradation mechanisms.

## *Introduction*

Formaldehyde (HCHO) is a central component of atmospheric chemistry. It is an intermediate gas in the oxidation of hydrocarbons in the troposphere [Meller and Moortgat, 2000]. Oxidation of Methane provides a global and constant source of HCHO. In addition to this constant background, the oxidation of non-methane hydrocarbons (NMHC) provides local sources of HCHO over continental boundary layers. As HCHO has a lifetime of only a few hours, these emissions are an important indicator of anthropogenic hydrocarbons emissions in the troposphere [Chance et al, 2000]. Formaldehyde is also a primary product of biomass burning and fossil fuel combustion. Elevated levels of HCHO are related to the releases by forests (e.g. ethene, isoprene, and methane), biomass burning, traffic and industrial emissions. Removal of HCHO is done by reaction with OH and photolysis. The photodissociation of HCHO participate to CO and $NO_2$ production [Jacob, 2000].

## *HCHO total columns retrieved from GOME measurements*

Vertical columns amounts of HCHO are determined in a two-step procedure. First, slant columns densities are retrieved using the Differential Optical Absorption Spectroscopy technique (DOAS) [Platt, 1994]. Second, a combination of the radiative transfer model DISORT [Stamnes, 1988] and results from the IMAGES global 3-D model [Muller and Brasseur, 1995] is used to determine the appropriate altitude-resolved air-mass factors (AMFs) which convert the fitted slant columns to vertical column abundances.

## DOAS retrieval of HCHO SCDs

The DOAS method consists in fitting, using non-linear least-squares routines, the (GOME) atmospheric spectra to a set of molecular absorption cross-sections measured in the laboratory. The spectral analysis is performed using WinDOAS, a multi-purpose DOAS analysis software developed over the nineties at BIRA-IASB.

The inversion of HCHO SCDs is performed in the 337.5-359 nm spectral range. The measured GOME spectra are adjusted to a Fraunhofer reference spectrum degraded to the GOME spectral resolution. HCHO fitting routines use reference spectra for HCHO, BrO, $O_3$, $NO_2$, $O_4$ and the Ring effect. The HCHO absorption cross-section used is from [Cantrell, 1990] (293 K). The temperature dependence of the $O_3$ absorption cross-sections is accounted for by fitting two cross-sections. I0-corrections are applied to $NO_2$ and $O_3$ reference spectra as well as a spectral shift of 0.03 nm. Ring spectra are generated by rotational Raman scattering calculation using a GOME solar irradiance as the source spectrum. A polynomial of order 5 is applied to remove the low-frequency features. The DOAS procedure accounts also for the GOME undersampling and an offset correction.

The fitting of HCHO encounters several difficulties:

- Due to the weak absorption features the signal to noise ratio is poor, and the retrieval is more sensitive to spectral interferences as well as to an accurate calibration of the measured spectra.
- There are strong interferences with Ozone and BrO absorptions.
- Due to the well know GOME diffuser plate artefact [Richter, 2001], using GOME solar irradiances as reference for the DOAS fit leads to an offset of roughly 1e16 mol/cm² in the HCHO slant columns, this offset shows great variations with solar day, going from 0.5e16 to 1.5e16 mol/cm².

In order to minimize these effects:

- BrO is fitted in a separated window (344.7-359 nm), and then imposed in the fitting window of HCHO. This technique minimizes the errors on the fit and removes BrO features in the HCHO columns.
- Ozone interference leads to artificial latitudinal dependency of HCHO columns, which varies with season. A correction is applied afterwards based on the assumption that HCHO background is constant over the Pacific Ocean [200° 220°] and along latitudes. This method is usually called reference sector method.
- Each day, a radiance spectrum is selected in the Pacific Ocean, where the background of formaldehyde is supposed to be constant and only due to methane oxidation. Using an earth-shine instead of the solar irradiance as reference provides more realistic residual and cancels the GOME diffuser plate artefact, but this introduces the problem of an unknown amount of HCHO in the background measurement. Columns are scaled to the HCHO values of the IMAGES model over the Pacific Ocean.

Fitting errors are lower than 4e15 mol/cm². Overall accuracy is determined by adding 5% uncertainty for the HCHO cross-section and 3% error for temperature variations of 30K in the troposphere.

## SCDs to VCDs, AMFs calculation

AMFs are calculated with a radiative transfer model (DISORT). It solves the radiative transfer equation for a pseudo-spherical atmosphere with multiple scattering. The use of altitude-resolved AMFs (or weighting function) allows separating the vertical dependence of the observational sensitivity to HCHO (calculated with a radiative

transport model) from the shape of the vertical profile of HCHO concentration (calculated with an atmospheric chemistry model). The resulting AMF is the product of the weighting function with the HCHO profile interpolated on the same altitude grid. Figure 1 shows the mean HCHO vertical column for the whole year 1997. For each GOME ground pixel, an AMF is determined as the product between the weighting function interpolated in the look-up table and the HCHO vertical profile determined by the IMAGES model for the given observation conditions. No selection or correction based on clouds has been applied. First tests tend to show that this lead to a slight overestimation of the HCHO columns.
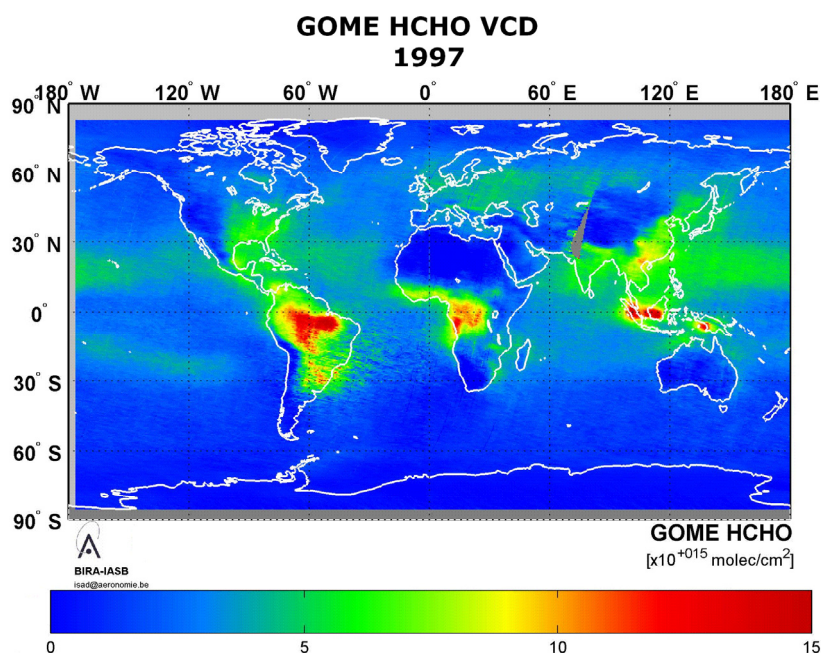


Figure 1: Yearly Mean HCHO VCD (1997)

## *IMAGES model*

IMAGES is a global three-dimensional chemical transport model of the troposphere that provides the global distribution of 59 chemical constituents between the Earth's surface and the pressure level of 50 hPa or approximately 22.5 km of altitude [Müller and Brasseur, 1995]. IMAGES is run at a resolution of 5 in latitude and longitude with 25 vertical levels and a time step equal to 6 hours. It simulates the concentrations of 40 long-lived (transported) and 19 short-lived chemical compounds through a chemical mechanism including 133 gas-phase reactions, 29 photodissociations, and 3 heterogeneous reactions on the surface of sulfate aerosols. For more details, see [Muller and Stavrakou, 2005].

## Comparison of IMAGES profiles with aircraft measurements

Tropospheric data from a number of aircraft campaigns compiled by [Emmons, 2000] are used as independent observations to be compared to IMAGES HCHO profiles. The data set provides regional profiles of aircraft observations of tropospheric ozone and its precursors, including formaldehyde. The observations and model concentrations are averaged in large regions with a 1-km vertical resolution. Images profiles are in blue and aircraft profiles in red. The relative AMF differences resulting from differences in HCHO profiles are indicated on each plot [%].
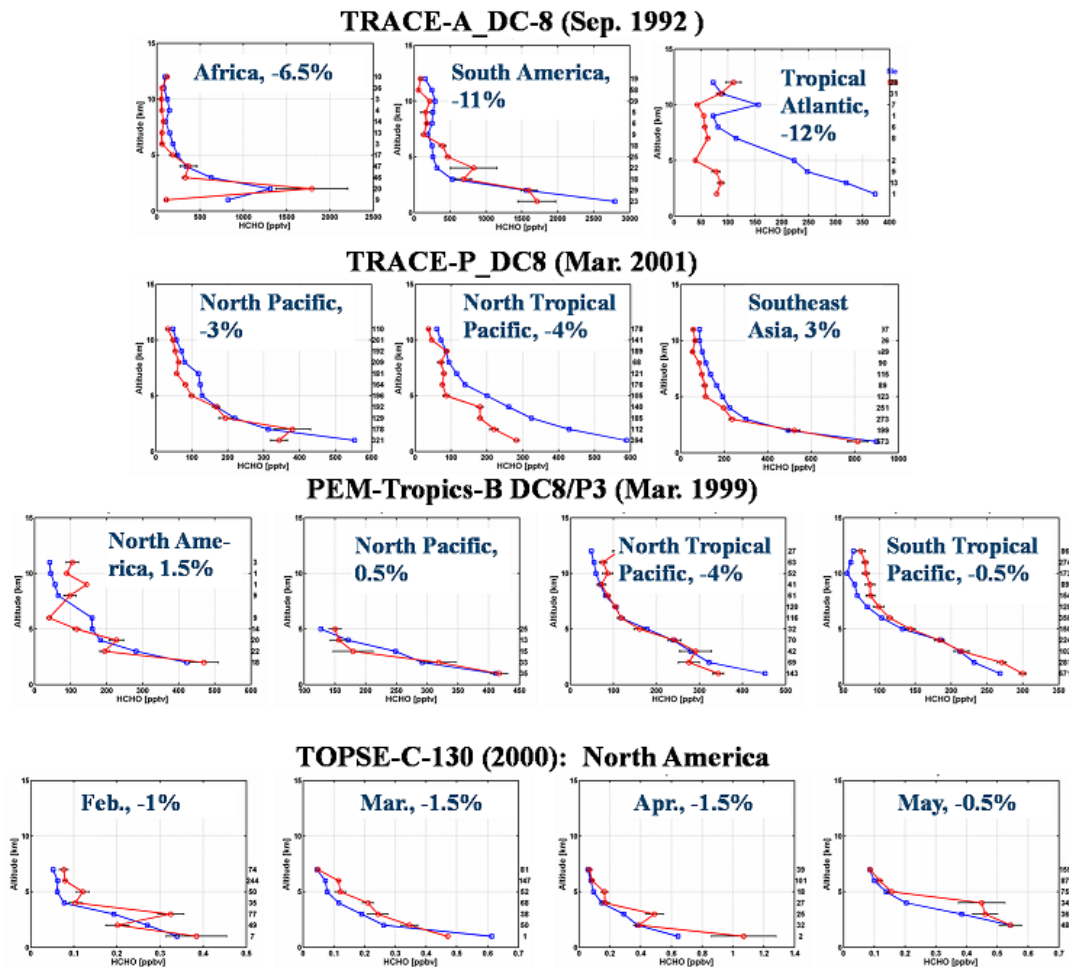
**Figure 2: Comparisons of IMAGES HCHO profiles with aircraft measurements.**

## Comparison between GOME and IMAGES HCHO columns

Figure 3 and Figure 5 compare GOME HCHO retrievals with the results of the IMAGES global CTM using newly updated biogenic emissions of isoprene and terpenes (MEGAN model [Guenther, 2005]) as well as methanol [Jacob, 2005] and other non-methane organic compounds. Biomass burning emissions are derived from the GFED inventory [Van der Werf, 2003] for the year 1997. In Figure 5, both the model results and GOME retrievals are averaged over large regions shown in Figure 4.

The comparison shows

- a remarkable agreement regarding the timing of the maximum associated to biomass burning in Tropical regions (Africa, Indonesia, Amazonia) and to biogenic emissions over China and the Eastern United States
- an overestimation of the model columns in Tropical regions outside the burning season, indicating that either biogenic emissions or the formaldehyde yield from isoprene and terpenes could be overestimated in these regions
- an indication that biomass burning emissions could be too low over Africa and Indonesia
- a severe discrepancy over Northern Africa and Australia, where the GOME retrieval are likely to be largely underestimated
- an underestimation of the modelled columns during wintertime at mid-latitudes, possibly related to the presence of snow.
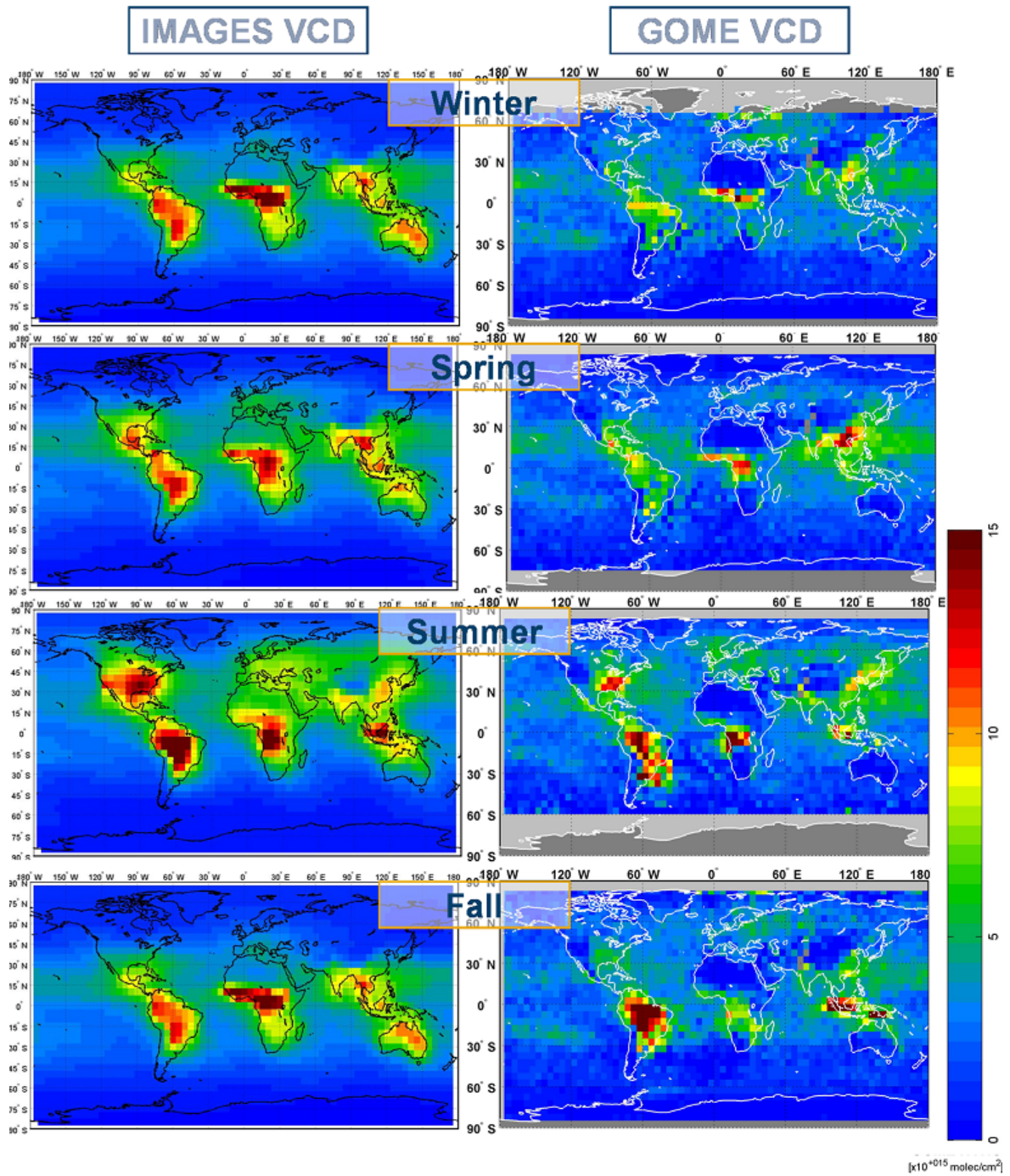
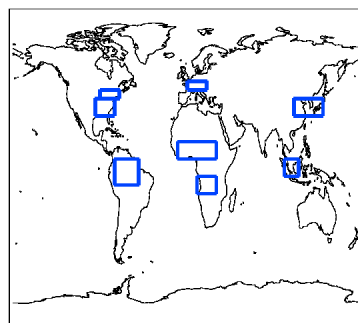**Figure 3: Comparison of HCHO seasonal mean between GOME (at 5° resolution) and IMAGES (1997)**



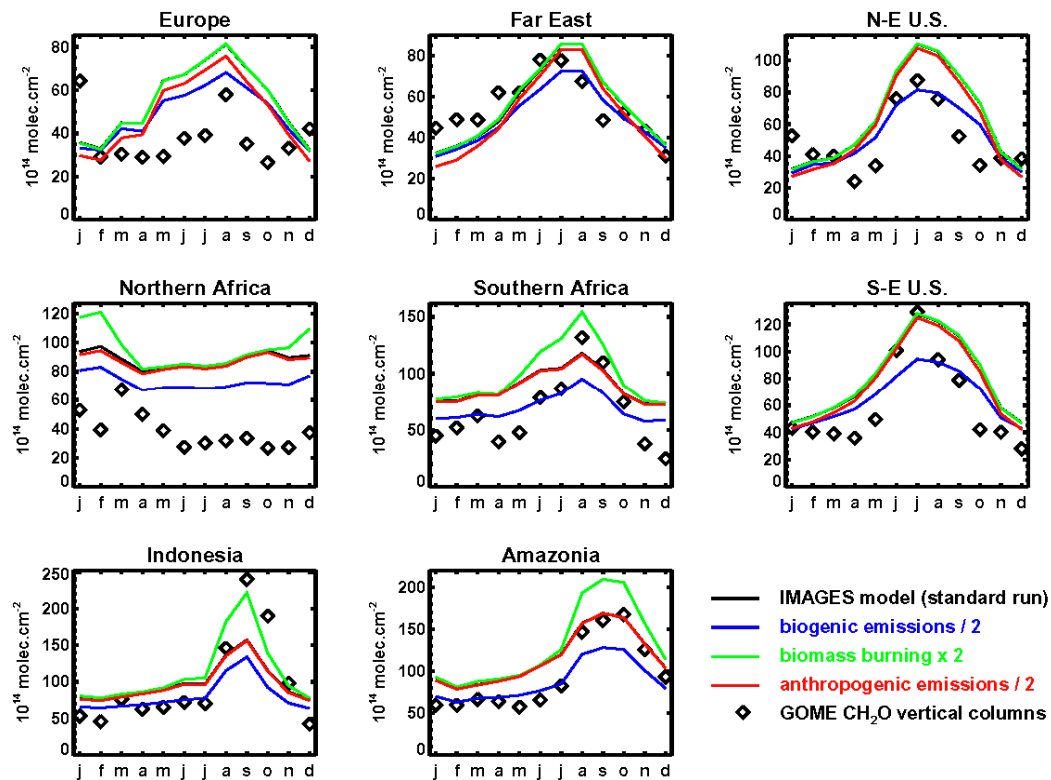**Figure 4: Regions used to average the HCHO values**

**Figure 5: Comparison of Monthly Mean GOME HCHO VCD with the IMAGES model (1997)**

## *Conclusion*

GOME and IMAGES HCHO columns show a very good agreement in time but satellite data seem to be lower than the model values. Future work will focus on the effect of clouds and aerosols on HCHO retrieval and the relation between the low HCHO values above deserts and the lower vegetation index. HCHO columns will be used jointly with MOPITT CO columns to constrain the emissions of CO and the NMVOCs, based on an inverse modelling framework described in more detail in the poster of Müller and Stavrakou (Big-region vs. grid-based approach for inverting the emissions of CO using MOPITT data).

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