

RETRIEVAL OF FORMALDEHYDE COLUMNS FROM GOME AS PART OF THE GSE PROMOTE AND COMPARISON WITH 3D-CTM CALCULATIONS.

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1. ABSTRACT

Formaldehyde (HCHO) is a central component of tropospheric chemistry. First it constitutes an important indicator of hydrocarbons emissions in the troposphere. Second, its photodissociation also plays a key role in the production of CO and NO₂. Through quantification of the global abundance of formaldehyde using satellite instruments, one expects to provide new constraints on the emissions of non-methane VOCs (NMVOCs) as well as on the budget of CO, which play a key role in the budget of tropospheric ozone and the hydroxyl radical OH. Formaldehyde is a product of the air quality service of the PROMOTE project (ESA GMES Service Element Atmosphere) and of the Dragon project “Air quality monitoring and forecasting in China”.

In the present study, global distributions of formaldehyde columns are derived from GOME for the years 1996 to 2001. The retrieval process is based on a slant column fitting using the differential optical absorption spectroscopy technique (DOAS), followed by a conversion to vertical column using appropriate air mass factors (AMFs). For the latter step, chemistry-transport models provide best-guess profiles of HCHO, based on the latest emission inventories, atmospheric transport, photochemistry, and wet/dry removal processes. We focus on a discussion of the main error sources that affect the retrieval of both HCHO slant and vertical columns.

Comparison with tropospheric chemistry models (IMAGES and TM5) are used to investigate the geophysical consistency of the retrieved columns. Furthermore, GOME HCHO is used to investigate the sensitivity of the global HCHO column distributions to changes in anthropogenic, biogenic and pyrogenic NMVOC emissions as well as on potentially uncertain parameters in their degradation mechanisms in the IMAGES model.

2. INTRODUCTION

Formaldehyde (HCHO) is the most abundant of the carbonyl compounds in the atmosphere. It is found both in the remote background atmosphere and in polluted urban atmospheres. In the background troposphere, the methane oxidation is the dominant formaldehyde source. In continental areas, formaldehyde is generated from the oxidation of biogenic hydrocarbons, such as isoprene and terpenes and from the oxidation of anthropogenic hydrocarbons. It is also anthropogenically generated directly from incomplete combustion processes, both from biomass burning and from internal combustion engines. It constitutes an important indicator of hydrocarbons emissions in the troposphere.

HCHO is a short-lived molecule. Its oxidation by OH radicals generates the hydro peroxy radical (HO₂) which reacts with NO producing NO₂, a precursor of tropospheric O₃. HCHO is also photodissociated to form HCO, which reacts with oxygen to form CO. As a source of CO, HCHO plays an important role in the global budget of CO in the natural troposphere. In both cases, HCHO exerts an influence on the oxidizing capacity of the atmosphere.



The quantification of the global abundance of formaldehyde using satellite instruments might help better constraining the emissions of non-methane VOCs (NMVOCs) used in current state-of-the-art chemical transport models (CTMs). It might also reduce uncertainties on the budget of CO, which play a key role in controlling the abundance of tropospheric ozone and OH, the hydroxyl radical. Finally, formaldehyde is an interesting indicator for biomass burning, rice fields and industrial activities.

3. HCHO TOTAL COLUMNS RETRIEVED FROM GOME MEASUREMENTS

Vertical column amounts of HCHO are determined in a two-step procedure. First, slant column densities are retrieved using the Differential Optical Absorption Spectroscopy technique (DOAS) [1]. The fitting process determines the slant column amount that minimizes the chi square error between observed and calculated GOME radiances. Second, a combination of the radiative transfer model DISORT [2] and profiles from the IMAGES global 3-D CTM [3,4] are used to determine the appropriate air-mass factors (AMFs) which convert the fitted slant columns into vertical column abundances. Vertical profiles of HCHO are sampled from IMAGES at the time and location of each GOME observation.

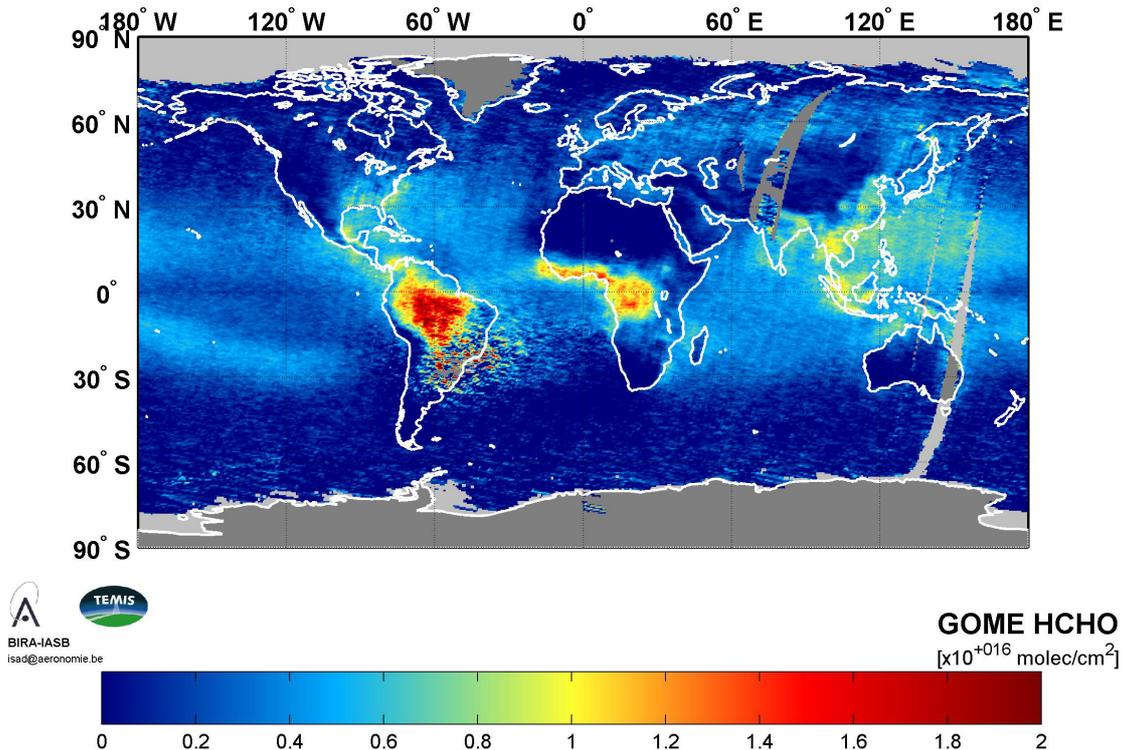


Fig. 1. GOME HCHO VCD – 1997-2001 – Cloud fractions < 20%.

3.1. DOAS RETRIEVAL OF HCHO slant column densities

The DOAS technique used in this work relies on an analysis of the characteristic absorption features of HCHO in the UV region. The method consists in fitting, using non-linear least-squares routines, the (GOME) atmospheric and solar reference spectra to an appropriate 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. This software, initially developed for ground-based applications, has been thoroughly validated through participation at various intercomparison exercises [5].

The inversion of HCHO slant column densities (SCDs) is performed in the 337.5-359 nm spectral range. The measured GOME spectra are adjusted to a Fraunhofer reference spectrum [6] degraded to the GOME spectral resolution. HCHO fitting routines use reference spectra for all absorbers present in the fitting interval, i.e. HCHO, BrO, O₃, NO₂, O₄ and the Ring effect. The HCHO absorption cross-section is from Cantrell (293 K) [7]. The linear temperature dependence of the O₃ absorption cross-sections is accounted for by fitting two cross-sections. Solar I₀-corrections [Alliwell et al., 2002] are applied to NO₂ and O₃ reference spectra as well as a spectral shift of 0.03 nm. Ring spectra are generated by convolution of a GOME solar irradiance with rotational Raman scattering cross-section of molecular nitrogen and oxygen [8]. A polynomial of order 5 is applied to remove the low-frequency

features. The DOAS procedure also accounts for the GOME undersampling [9] and an offset correction. In order to minimize the interferences between BrO and HCHO absorptions, BrO is fitted in the wavelength range 344.7-359 nm. This technique improves the fits, minimizing the residuals and removing BrO features in the columns of HCHO. The well known GOME diffuser plate artifact causes variation of the solar spectra with the solar angle [10]. These variations interfere with the spectral retrieval in the fitting window of HCHO. This causes important daily offset in the background values of HCHO (ranging from 1 to 3×10^{16} molec/cm²). This effect cannot be avoided and consequently HCHO values from GOME retrieval will always be differential. A normalization is performed such as the background HCHO is zero at equator. The GOME HCHO columns show a strong latitudinal dependency, with generally two maxima in the tropics, a strong decrease with the solar zenith angle (SZA) and finally an increase at very high SZA. Comparing with CTM values, we can infer that part of this variation is likely to be real, however the decrease with SZA is too important to be fully explained by the model and the final increase certainly is an artefact. Tests on synthetic spectra have shown that Ring effect and the strong ozone absorption are the two main causes of errors on the retrieval of HCHO SCDs. They have opposite effects, ozone causes and overestimation of HCHO at high SZA (3×10^{15} molec/cm²), while the Ring effect causes an underestimation of HCHO which increases with SZA (up to 9×10^{15} molec/cm²) but which is already significant at low SZA (1×10^{15} molec/cm²). Overall, the DOAS retrieval under-estimates the HCHO columns by an amount that ranges from 1×10^{15} molec/cm² and 6×10^{15} molec/cm² at high SZA. The residuals of the fits are dominated by the currently imperfect Ring effect correction. As these effects could not be fully corrected in the existing GOME product, the mean latitudinal variation of HCHO was empirically adjusted on the model variation. With this procedure one obtains realistic background HCHO columns but to the expense of a loss of the information contained in the satellite observations. In order to get rid of the latitudinal correction applied to the satellite retrieval, better Ring correction schemes must be designed. One can also note in Figure 2 that the two CTMs IMAGES and TM4 do not have the same HCHO background value. This highlights the remaining uncertainties concerning formaldehyde and the need to collect more information about its absolute columns.

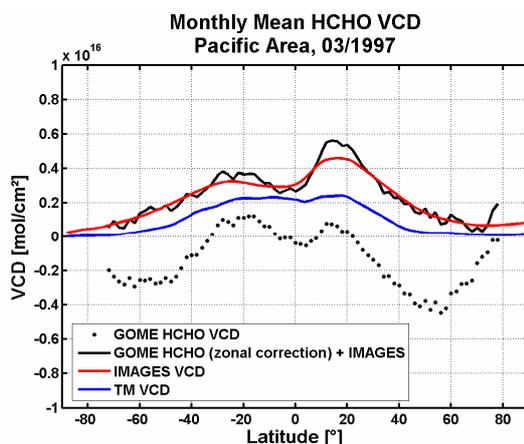


Fig. 2. Zonal variation of the background formaldehyde as seen by GOME and CTM.

3.2. AMFS CALCULATION

The second step in the retrieval is the determination of the air mass factor (AMF) used to convert slant columns into vertical columns. The AMF is defined as the ratio of the slant column to the vertical column, and depends on the radiative transfer properties of the atmosphere. In this work, altitude-resolved AMFs (or weighting functions) are calculated with the radiative transfer model DISORT [2]. DISORT solves the radiative transfer equation for a pseudo-spherical atmosphere with multiple scattering. The HCHO AMF is approximately half the geometric AMF for typical conditions, in the absence of snow or ice cover. Scattering thus decreases the sensitivity of GOME to atmospheric HCHO by about a factor of 2 [11]. The use of weighting functions allows separating the vertical dependence of the GOME observational sensitivity (calculated at 350 nm with DISORT) from the shape of the HCHO vertical profile (inferred using an atmospheric chemistry model). HCHO vertical distributions are taken from the IMAGES CTM. IMAGES describes 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 [3]. It is run at a resolution of 5

degrees in both latitude and longitude, over 40 vertical levels and a time step equal to 6 hours. It simulates the concentrations of 40 long-lived gases (transported) and of 19 short-lived species [4]. The resulting total AMF is the product of the HCHO concentration profile by the calculated weighting function and normalized by the vertical column:

$$AMF = \frac{SCD}{VCD} = \frac{\sum_l amf_l * P_l}{\sum_l P_l}$$

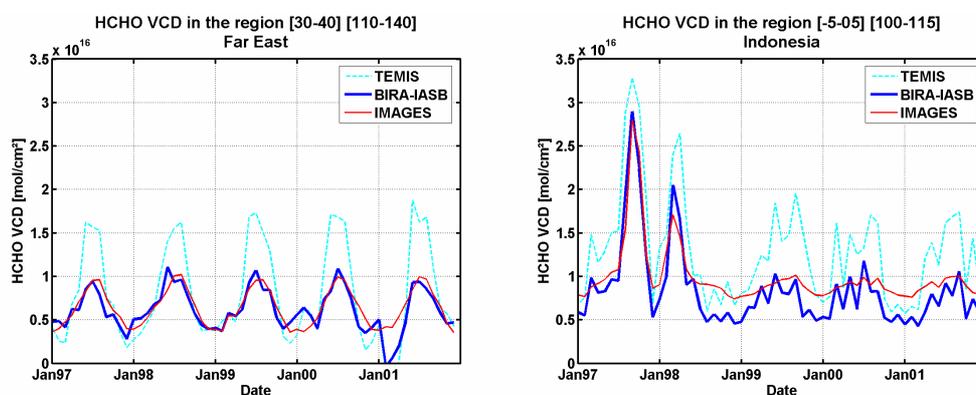
In this equation, amf_l and P_l are respectively the values of the weighting function (unitless) and of the HCHO profile (in molec/cm³) at layer l . Note that only the shape of the profile is important. For each GOME pixel, the weighting function is interpolated in a look-up table according to the local surface properties as well as sun and viewing geometries. Parameters taken into account are the solar zenith angle, the viewing angle, the relative azimuth angle, the surface elevation and the albedo. At the same time, for each GOME pixel, best-guess profiles of HCHO are interpolated from a table of IMAGES HCHO profiles. IMAGES calculations take into account updated emission inventories, atmospheric transport, photochemistry, and wet/dry removal processes of the corresponding year, month and location [4]. In order to reduce the impact of clouds on the retrieved HCHO columns, only the pixels having a cloud fraction less than 20 % are selected.

4. REGIONAL MEAN

For different regions where formaldehyde is observed from biogenic emissions and biomass burning, time series of GOME retrievals and model calculations are presented. These results are compared with vertical columns (VCDs) derived using another source of modeled HCHO profiles (the 3D-CTM TM5). It appears that differences in the HCHO profile shapes simulated by the two models have a large impact on the total AMF. This causes differences in vertical columns of up to 60 % above regions of emissions. Good knowledge of the profile is thus very important to obtain a realistic total column from satellite.

4.1. HCHO PROFILES AND THEIR INFLUENCE ON THE GOME HCHO VCDs

GOME HCHO retrievals are compared with results from the global CTM IMAGES that uses newly updated biogenic emissions of isoprene and terpenes [13], as well as methanol [14] and other non-methane organic compounds. Biomass burning emissions are derived from the GFEDv2 inventory [15]. BIRA-IASB VCDs obtained using IMAGES profiles for the calculation of the AMFs are plotted against VCDs obtained at KNMI from the same SCDs but using AMFs calculated from TM5 profiles [16] (TEMIS results, see fig. 3.). TEMIS VCDs appear to be substantially larger than BIRA-IASB ones. Differences between VCDs are caused by differences between CTM profile shapes. As can be seen on fig. 4., TM5 profiles are peaking much closer to the surface than IMAGES ones. This has a large impact on the total AMF and can lead to differences of up to 60 % above regions of large emissions. HCHO profiles need to be further validated by independent measurements.



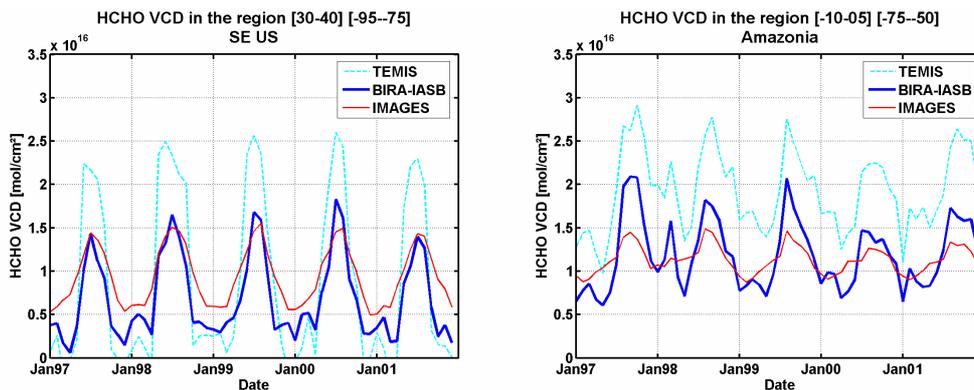


Fig. 3. HCHO VCD above biogenic (SE US, Far East) and biomass burning regions (Indonesia, Amazonia)

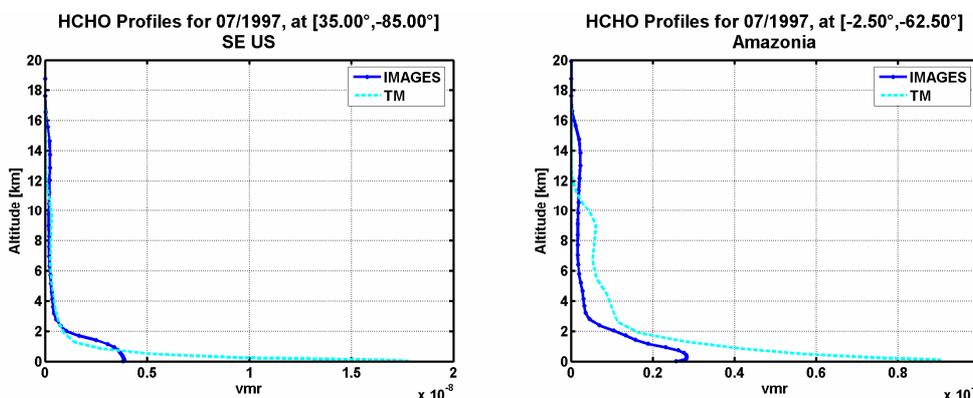


Fig. 4. HCHO profiles above biogenic (SE US) and biomass burning regions (Amazonia)

4.2. VALIDATION OF IMAGES PROFILES USING AIRCRAFT MEASUREMENTS

Tropospheric data from a number of aircraft campaigns compiled by Emmons et al. (2000) are used as independent observations for comparison with IMAGES HCHO profiles [12]. The data set provides regional profiles of tropospheric ozone and of its precursors, including formaldehyde. The observations are averaged onto a 5×5 horizontal grid with a 1-km vertical resolution. The data files, including the statistics of the data sets (number of measurements, minimum, maximum, mean, standard deviation) can be accessed through the data composites web site (http://acd.ucar.edu/_emmons/DATACOMP/camp_table.htm). The model concentrations are averaged in the same regions taking into account the location of the measurements and the number of measurements at each location. The IMAGES results are in very good agreement with aircraft measurements, in particular over Pacific Ocean where we can observe the background of formaldehyde.

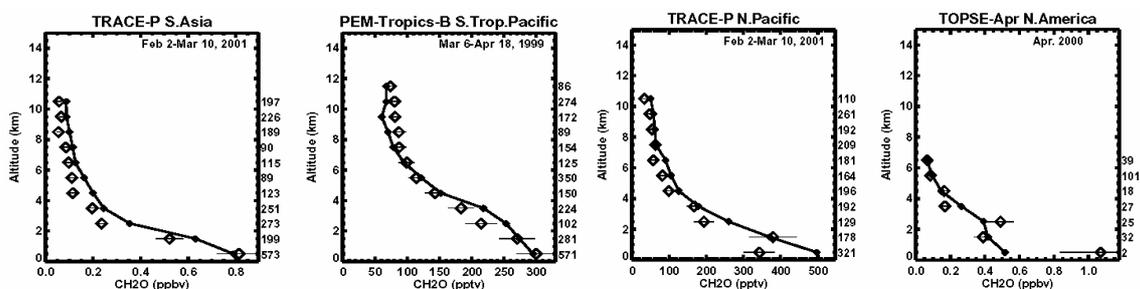


Fig. 5. IMAGES – Aircraft HCHO profiles

5. CONCLUSIONS

The comparison of the GOME retrieved HCHO vertical columns with results from the IMAGES CTM shows a remarkable agreement as regards the levels of emissions associated to biogenic emissions over China and the Eastern United States. The emissions associated with biomass burning in Tropical regions (Africa, Indonesia, Amazonia) show a good agreement regarding the timing of the maximum levels. However, we can note 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. There is also an indication that biomass burning emissions could be too low over Amazonia. We find a severe discrepancy over Northern Africa and Australia, where the GOME retrievals are likely to be underestimated due to unresolved slant column fitting artifacts in these regions.

The shape of the profile used to calculate the total air mass factor can introduce differences in the vertical column of up to 60%. This shows the need to validate model profile and satellite data with independent measurements.

In the near future, 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.

6. REFERENCES

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