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Atmospheric Chemistry and Physics Discussions

Interactive comment on "GOME-2 observations of oxygenated VOCs: what can we learn from the ratio glyoxal to formaldehyde on a global scale?" *by* M. Vrekoussis et al.

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We would like to thank both reviewers for their positive comments and suggestion which helped to improve our manuscript. Below we give the responses to comments point by point and describe the modifications made to the manuscript.

Responses to reviewer 1:

Abstract (line 11): Typo, misplaced ')' after tropical forests (Corrected).

Introduction(Page 19033, line 9): Typo, 'access' should be replaced by 'assess' (Corrected).

Introduction (Page 19033, line 21): The Amazon rainforest is 'remote' but can have high HCHO (>10ppb) mixing ratios. Do the authors mean 'remote marine atmosphere.

Reply: Indeed it was meant remote marine atmosphere (Corrected).

Introduction (Page 19034, line 6): Primary sources may be considered small (or negligible) on a global scale but can have a large effect regionally and locally.

Reply: This is true depending on the area. The sentence has been rephrased to "Despite its local and/or regional importance, the contribution of the primary sources, on a global scale, is considered to be small or negligible in comparison to the large secondary sources mentioned before".

The GOME-2 Instrument (Page 19036, line 9): Typo, replace 'nearly' with 'near' (corrected).

Methods – Data retrieval (Page 19037, line 18): The author's state there was no further correction for residual clouds. However, in the air mass factor (AMF) calculation, are AMFs computed for both clear and cloud conditions (based on retrieved cloud properties) so that the final AMF is weighted combination of both (i.e. as proposed by Martin et al, JGR, 2002 doi:10.1029/2001JD001027)?

Reply: Measurements were cloud-screened in order to minimize the biases from the cloud shielding. A simple cloud screening algorithm based on the intensity criterion has been used for the selection of data with a cloud cover below a given number. The consistency of this method has been successfully checked with the results of the FRESCO cloud cover product (Koelemeijer et al., 2001). For this study the selected threshold was 20% in order to avoid large data gaps and no explicit cloud correction has been applied for the residual clouds. The presence of clouds may impact on the ratio R_{GF} in two ways: first, if the vertical profile of the two species is different, the

relative importance of the shielding and enhancement effect of clouds on the fraction of the absorber below and above the cloud is different leading to a change in R_{GF}. Second, even if the vertical profiles are the same, the wavelength dependence of surface reflectance and scattering efficiency leads to slightly different effects for HCHO and CHO.CHO which are retrieved in different spectral ranges. This can in principle be corrected using cloud information and vertical profiles from models as proposed in Martin et al. (2002) for NO_2. However, in the absence of good information on the vertical profiles of HCHO and CHO.CHO on a global scale, we feel that such a correction would actually increase the uncertainty in the analysis. We expect to refine retrievals and reduce any systematic error, as better information on cloud becomes available.

Methods – Data retrieval: How is the R_{GF} affected by (a) differences in the shape of the HCHO and CHO.CHO profiles and (b) their relative vertical distribution to aerosols? Can a lot of the variation in the R_{GF} (which is very sensitive) be explained by aerosols impacting the photon light path?

Reply: (a) For the current study the AMF computation of both species is based on the selection of the same profile shapes and types (urban, biogenic and rural, see Wittrock, 2006) because 1) HCHO and CHO.CHO have similar sources and sinks and 2) there is sufficient literature information only on the HCHO profile (e.g. Fried et al., 2003; Singh et al., 2004; Heckel et al., 2005) but almost no information on the CHO.CHO profile. In reality small differences may exist in the shape of the vertical profiles of CHO.CHO and HCHO mainly because HCHO has an additional unique source; the oxidation of methane by the OH radicals. For this reason and although in our view the assumptions for the present are reasonable we need to extend our knowledge on the shape of the vertical profile of glyoxal over various sources. In the case that the assumption of similar HCHO and CHO.CHO profiles is not correct, the VCDs and therefore the ratios will be affected. (b) Likewise, if there are no systematic differences in the HCHO and CHO.CHO profiles it is expected that changes of the vertical distribution to aerosols will have only small impact on the R_{GF} ratio. If this assumption is drastically not valid,

changes in aerosols could have an impact on the computation of the vertical columns of HCHO and CHO.CHO; the aerosol vertical distribution in addition to the aerosol type (e.g. urban vs. maritime) affect the visibility and subsequently the photon light path. The visibility depends on the wavelength dependence of the aerosol extinction coefficient which in turn will affect the retrievals of HCHO (uv spectral region) and CHO.CHO (vis spectral region). However, given the lack of information on the vertical distribution of aerosols and CHO.CHO, any attempt of a correction for aerosol effects would be speculative at this point.

Global picture of HCHO and CHO.CHO (Page 19038, line 5): How have these composite maps (or rather two-year averages) been produced? What was the grid resolution, and what data filtering or smoothing has been applied?

Reply: These maps (Figure 1) are based on the averaging of the 24 individual months starting from January 2007 and ending to December 2008. Data gridded to 0.5^ox0.5^o have been used for the following analysis and no further filtering or smoothing has been applied.

Global picture of HCHO and CHO.CHO (Page 19038, line 16): Surely high HCHO columns (>2x10^{16} molecules cm^{-2}) must be observed over the south eastern US in summertime? These cannot be considered 'moderate'.

Reply: The term moderate is used in comparison to the annual higher VCD_{HCHO} values observed over the tropical and biomass burning affected regions. The south east USA source is large compared to Europe and rest of USA, but small compared to the above mentioned sources. As correctly pointed out by the reviewer, over the south eastern US in summertime values can exceed the 2x10^{16} molecules cm^{-2}. However the presented maps depict the annual VCD_{HCHO} and not the seasonal one.

Comparison of GOME-2 and SCIAMACY values (Page 19039, line 26): Why was 20S

chosen as the southern limit?

Reply: The reason of this choice depends mainly on the poorer retrievals due to lower signal to noise ratio encounter at high SZA and due to the interference of formaldehyde with ozone and to some extend with BrO as they are the dominant absorbers at these latitudes. For these latitudes the chi-square values of the fit are higher in comparison to northern latitudes resulting to less trusted VCD$_{HCHO}$ results.

Comparison of GOME-2 and SCIAMACHY values: Why is the poorest agreement consistently over Europe?

Reply: One of the basic reasons for the poorer agreement over Europe is the cloudiness. The selected region over Europe is found at higher latitudes in comparison to the other selected locations and is dominated by a higher cloud fraction. That leads to fewer accepted measurements over Europe and subsequently higher uncertainty. Additionally for both species the VCD values are at the lower range of their variability. That means that the uncertainty based on the systematic errors will have a greater impact in comparison to the higher values. There are a couple of additional factors determining the AMFs and contributing in the aforementioned poor agreement; for example the surface anisotropy is high for Europe (Zhou et al., 2010) and the fraction of the photons penetrating the atmosphere is lower at larger SZAs.

Ratio R$_{GF}$ – "CHO.CHO to HCHO" (Page 19041, line 11): The sentence: "In addition it was observed that regions characterized as polluted (e.g. northeast China) experience lower R$_{GF}$ values than those dominated by influence." is confusing, i.e. dominated by the influence of what? I assume pollution but please make it clearer.

Reply: The word biogenic was added: In ... dominated by biogenic influence.

Ratio R$_{GF}$ – "CHO.CHO to HCHO" (Page 19041, line 41): Are there any seasonal patterns in the R$_{GF}$, or is the data too noisy so that only yearly means can be interpreted?

Reply: To perform a seasonal analysis on the ratio more values are needed. The seasonality of the R$_{GF}$ mainly under biomass burning conditions is going to be exploited in a forthcoming study when a large enough sample of GOME-2 OVOC data will be available.

Error Analysis (Page 19042, eqns 1 and 2): Please clarify how are 'x' and 'y' determined? What is the error on these terms?

Reply: X and Y are error terms by themselves contributing to the total error; both are ground scene dependant. In other words, they depend on the individual ground scene cloudiness, surface albedo and aerosol load and on a monthly basis they vary from between 10% and 30% of the given VCD value.

Error Analysis (Page 19042, eqn 3): Is there an equal sign missing? For example should this read: R$_{GF}$ = [CHO.CHO]/[HCHO] = a / b

Reply: The equal sign has been added to the text.

Error Analysis (Page 19042, line 19): Is the spatial resolution of the coarse grid equal to D multiplied by the spatial resolution of the finer grid?

Reply: The text has been modified to: However, ... reduced by $\sqrt{}$((1/(DxD)) (where D is the ratio of the coarse to fine spatial resolution) and $\sqrt{}$((1/n)) (temporal resolution is n months).

Error Analysis (Page 19043, lines 13-21): This last paragraph is slightly confusing in terms of how they have calculated the errors. Could the authors make this clearer?

Reply: First of all in order to describe a more realistic-representative ground scene we changed the "old" VCDs with the following ones: VCD$_{HCHO}$=7.00·10^{15}molec cm^{-2} and

$VCD_{CHO.CHO}$= 3.0·10^{14}molec cm^{-2}. The error in this case is almost identical to the one presented before. The text was changed as follows:

The total error will comprise the random and the systematic error; for a time period of two years, 2007-2008, and for a typical ground scene where VCD_{HCHO}=7.00·10^{15}molec cm^{-2} and $VCD_{CHO.CHO}$= 3.0·10^{14}molec cm^{-2} the random error of the R_{GF} ratio as computed from Eq. 5 and based on the reduction of the HCHO and CHO.CHO uncertainties due to the temporal $\sqrt{}$((1/24)and spatial$\sqrt{}$((1/(4x4)) averaging used is equal to 0.003. The systematic error is not reduced as the random one; based on the aforementioned estimation (15%), the systematic uncertainty as computed from Eq.5 for the ratio is about 0.008. Thus the total uncertainty of the R_{GF} ratio (and not that of the individual species) is 0.011, which is about 31% and 22% of the typical values of 0.035 and 0.050 determined for a ground scene dominated by anthropogenic and biogenic emissions respectively (see sections 3.4.1 and 3.4.2).

Error Analysis (Page 19043, line 21): Typo, there are not any 3.4.1 and 3.5.2 sections.

Reply: The 3.5.2 has been changed to 3.4.2 (Corrected).

R_{GF} and emission sources (Page 19045, line 9): Please add an appropriate reference for the AATSR fire counts.

Reply: The link to (ATSR World Fire Atlas, http://dup.esrin.esa.int/ionia/wfa/index.asp) is added to the text.

R_{GF} and anthropogenic emissions (Page 19046, line 9): Again, could aerosols be influencing the ratio over urban areas instead of changes in HCHO and CHO.CHO production from their precursor emissions?

Reply: As explained above, the presence of urban aerosols is accounted for in the AMF calculations for both HCHO and CHO.CHO. As long as the aerosol assumptions made

are realistic, any changes in the ratio of HCHO to CHO.CHO as a result of the different radiative paths between 437.5 nm and 360 nm are taken into account. Deviations from the assumed aerosol profile will have an impact on the R_{GF} as the reviewer points out. The magnitude and sign of the aerosol effect depends strongly on the type, AOD and vertical distribution of the aerosol (Alexandre et al., 2010) but in most cases is expected to vary only moderately between 360 and 437.5 nm. An explicit treatment of aerosol effects in the retrieval would be preferable but at this point is impossible due to the lack of reliable information on the aerosols present in the individual satellite observations.

R_{GF} and biogenic emissions (Page 19047, line 17): Isn't it how fast the emitted precursors are oxidized rather than 'more CHO.CHO is released to the gas-phase than HCHO'? I think this is slightly misleading.

Reply: Both could be true. Either the oxidation of the biogenic precursor species, mainly of isoprene and terpenes could favor glyoxal production or the remaining "net" glyoxal could be higher than HCHO. The text was modified, taking this point into account, to:

"The respective analysis disclosed a progressive increase of the R_{GF} with increasing EVI indicating that either the oxidation of the biogenic precursors such as isoprene and terpenes favors glyoxal production or more CHO.CHO remains in the gas phase than HCHO".

R_{GF} and biogenic emissions (Page 19047, lines 23-26): Typically as the EVI increases to larger values it is more representative of pristine and mostly forest covered regions. It should come as no surprise then that the NO_2 should decrease as well since the anthropogenic influence is much smaller (especially as the data have been filtered to remove the influence of biomass burning).

Reply: That is absolutely true. In theory this was expected and it was cross confirmed by the observations. We therefore see no reason to change the text.

Figures 5 and 6: Would be much improved in colour rather than B/W. Figure 6, parts c and f could be enlarged too.

Reply: Parts of figures 5 and 6 are now plotted in colour. Figure 6 has also been rearranged in respect to the size of panels c and f as requested. Moreover the respective explanations of the colour changes are adapted in the manuscript and in the figure captions.

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