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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 2:

Comment 1-Figure 3. The conclusions of this paper are centered around differentiating $R_{GF} > 0.4$ and $R_{GF} < 0.4$. It would greatly assist the reader if the plot of R_{GF} thus makes a clear color distinction at this threshold. I would suggest using a blue-white-red color scheme centered at 0.4. Use another color (e.g., grey) for areas without

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data.

Reply: Figure 3 was modified as requested. It is divided into two parts in order to incorporate the requested points highlighted in the current and the following comment. Figure 3a depicts the global land R_{GF} values centered at the 0.4 threshold. Values higher than 0.4 are plotted in blue and values lower than 0.4 are plotted in red. Grey colour has been used for the areas without data. In addition, R_{GF} values with large uncertainty due to e.g. large solar zenith angles, high altitude and high surface reflectivity, are filtered out. This data filtering was based on the cut-off of the R_{GF} values close to 0 and those which are greater than 0.1.

Comment 2. The authors clearly demonstrate that the significance of R_{GF} in many areas is driven by anthro vs. natural sources. However, there are many areas with substantial variability in R_{GF} that are not addressed at all in the paper, nor are they easily rationalized given the explanations provided for other areas. For example, there are wide regions of the globe where the ratio seems to have somewhat random pattern of high and low value (e.g. midwestern US, most of South America below 20^{o}S, central Australia, most of Russia, etc.). Certainly not all of these variations are indicative of anthro. vs. natural sources. I suspect that this ratio is only very meaningful where the absolute concentrations of either species are significantly large. Thus, I suggest that in Figure 3 the plot omit any areas where concentrations of one or both of the species are not above a threshold. Otherwise, please provide an explanation for the variability in these areas – is it lightning NOx or soil NOx? Why do areas with high altitude seem to have high R_{GF} ?

Reply: Indeed there are places around globe where the ratio shows large scatter and a random pattern. This is to a large extent attributed to the high uncertainty of either $VCD_{CHO.CHO}$ or VCD_{HCHO} or both due to their low values. There are several reasons for this data scattering: The HCHO retrieval at high latitudes is poorer due to spectral interferences from ozone and BrO. In addition, as SZA increases, the surface

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solar radiation decreases resulting in poorer signal to noise ratios. However these random patterns may hide, at least to some extent, meaningful information. For example around a region under intense biomass burning, a mixture of R_{GF} values is expected. For this reason, we chose to present the data in two panels. Panel a) as described before shows the global land R_{GF} values with only a few limitations. In addition, panel b) is based only on those VCD values which are not close to the detection limit of both species. The reduced data shows in a more clear way that the anthropogenically influenced areas experience R_{GF} values lower than 0.4 (red colour) and the naturally driven sources result in R_{GF} values higher than 0.4 (blue colour).

Comment 3. Section 2.5: The trend noted over the given set of cities is quite interesting, and is remarkably consistent within the set of cities selected. Yet, when looking at Figure 3, one wonders if only favorable locations were selected for inclusion in this analysis. I was wondering why cities such as Rio, Buenos Aires, Lima, or Mexico City, were not included. Does the trend break down in these areas, was the data just not available there for other reasons? Over how wide of an area is the trend significant? In other words, are the variations seen in places such as these, or others, such as France, Spain and England, truly indicative of anthropogenic vs natural land use? I think an easy test of the authors' assumptions would be to make a scatter plot of R_{GF} vs a relatively recent estimate of anthropogenic NOx emissions, as used in global chemical transport models, and see what fraction of the variability of R_{GF} can actually be explained by variability in the anthropogenic emissions.

Reply: For the selected trends we chose cities/regions with various NO_2 levels in order to check the variability of the R_{GF} ratio. Cities over which the retrieval of one or both species was poor were not selected. In particular, satellite observations for Mexico City are affected by the high altitude, the frequent inversion situations and the proximity of mountains and are considered to have higher uncertainty. Rio and Buenos Aires are found at lower latitude than the limit of 20^oS mentioned before; in addition their retrievals suffer from the South Atlantic Anomaly, which is when the instrument passes

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through the Van Allen belt. Finally Lima although not reported is consistent with the linear regression reported graph to Fig.7 with NO_2 values equal to $2.5 \cdot 10^{15}$molec cm^{-2} and ratio equal to 0.45. In general, the wider the emission area is the better the match with the satellite footprint. Concerning the last part of the comment on using the NOx emissions estimates; we constructed the plot of the EDGAR anthropogenic emissions of 2005 (including residential, industrial and transport activities) vs. the R_{GF} values. The general tendency of the R_{GF} values shows a decreasing trend with the increasing anthropogenic emissions. However the scatter of the data is too large to estimate the fraction of the variability of the R_{GF} which can be explained by the variability in the anthropogenic sources. The reason is that there are other effects contributing to the variability of the R_{GF} including biogenic emissions, measuring uncertainties etc .

Comment 4. Do recent papers on isoprene photochemistry (e.g., those from Paulot et al., Science 2009) affect the estimates of isoprene yields of HCHO and CHO.CHO?

Reply: This paper describes a very important study on the oxidation of isoprene via the formation of hyrdoxyhydroperoxides; almost 100 Tg/y of these species is expected to be emitted to the atmosphere. These epoxides have a short lifetime, they are drastically affected by the presence of NOx and their high yield formation can provide a suitable precursor for SOA formation from isoprene. At first glance it seems that the presence of such species will affect the yields of HCHO and CHO.CHO especially when glyocoaldehyde is being formed. However, the quantification of the formaldehyde and glyoxal yields from isoprene have to be checked with a global CTM model (e.g. with the GEOS-CHEM model used for the estimation of the distribution of these epoxides).

Comment 5-p19035: Could SOA serve as a CHO.CHO source owing to oxidation / volatilization of other compounds (e.g., Kwan et al., GRL 2006), rather than just reversible uptake of CHO.CHO itself?

Reply: Stavrakou et al. (2009) suggested that an unknown secondary source of glyoxal

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accounts for 50% of the global glyoxal budget. Given the fact that the current mismatch of models and measurements is considerably large, such a suggestion has to be carefully considered. However, more information should be acquired on the type of species that are oxidized or volatilized and their respective hydroscopicity. We added this reference to the manuscript (introduction section) as a potential source of glyoxal: "SOA may also serve as an independent glyoxal source via the oxidation or volatilization of other compounds (Kwan et al., 2006)".

Comment 6-p19049, 23: I was a bit confused when I read this line, as I thought the authors were attributing lower R_{GF} values to higher NOx levels rather than larger emissions of anthropogenic VOCs.

Reply: We think that here there was a misinterpretation of the text by the reviewer. The text refers to the concurrent observations of high VCD_{NO2} and low R_{GF}. The last sentence of the conclusion attributes this observation to the large emission of anthropogenic VOC's. However in order to avoid further misunderstanding we changed the word "as characterized" to "experience" as follows: It was found that regardless of geographical region, the more polluted cities of the study experience lower R_{GF} values than those above the less polluted cities. This is attributed to the larger emissions of anthropogenic VOC in such air masses.

Minor corrections abstract: missing a closing bracket in line 4 (corrected).

p19033, 23: "on its" (corrected).

p19033, 27: "2006)," (added).

p19040, 28: "by Spaulding" (corrected).

p19043, 24: change "confronted" to "compared"? (corrected).

p19048, 13: "rate oxidation" to "oxidation rate" (corrected).

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p19049, 22: “RGF” to “R_{GF} ” (corrected).

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