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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The influence of natural and anthropogenic secondary sources on the glyoxal global distribution" *by* S. Myriokefalitakis et al.

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We thank the reviewer for the careful reading and the thorough comments that helped improving our paper. We have taken all of them into account when revising the manuscript:

Simple calculations to derive the 'missing source strength' and additional simulations are included in the revised version with appropriate discussion and highlights are added in the abstract.

The discussion has been improved in the revised version to address the implication of the discrepancies between model results and observations. In particular, in the revised manuscript we now mention:

'The model results are compared with satellite observations of glyoxal columns. When accounting only for the secondary sources of CHOCHO in the model, the model underestimates CHOCHO columns observed by satellites. This could be attributed to an overestimate of glyoxal sinks or a potentially missing CHOCHO global source of about 20 Tg/y. However, consideration of primary emissions of CHOCHO over land from biomass burning and other anthropogenic combustion sources of about 7 Tg/y leads to an overestimate by the model of the observations over hot spot areas'(in the abstract).

'The impact of potentially significant anthropogenic primary sources of CHOCHO on its tropospheric columns has been investigated in one simulation that considers biomass burning and other anthropogenic combustion primary emissions to be 4.8 and 2.5 Tg/y respectively, i.e. almost 2 times (within the range given by Hays et al., 2002) higher than those of HCHO' (In section 2.1).

'Despite the significant variability in the primary CHOCHO emission factors and the scarcity of available data, the possible impact of significant primary sources of CHOCHO on its tropospheric columns has been investigated in an additional simulation (S4) that considers such emissions from biomass burning as well as from anthropogenic combustion sources proportional to those of HCHO.' (In section 2.3)

'Results from the simulation S4 accounting for potential primary sources of CHOCHO are also reported in Table 2 and indicate only minor improvement in the model comparisons with surface observations.' (In section 4.1)

'consideration of primary anthropogenic sources of CHOCHO further improves the general agreement of model results with satellite observations over land' (In section 4.2).

Results of S4 are now shown in Figures 1d, 1e, 2f, 3k and 3l as well as in table 2 and are appropriately discussed in the manuscript. In section 4.2 referring to the high CHOCHO columns over ocean we mention that: 'Figure 1c indicates that at least about 25% of the CHOCHO column is missing in the model when accounting for all data and their variability. Taking into account the global secondary source calculated by TM4-ECPL of 56 Tg/y this missing CHOCHO source corresponds to about 20 Tg/y that could be entirely or partially located over the oceans (see further discussion for the existence of primary land sources). Phytoplankton bloom areas could release significant amounts of VOC in the atmosphere. Such emissions are not taken into account in the present study. Note that this discrepancy could be also attributed to an overestimate of glyoxal sinks. Compared to the earlier simulations in Wittrock et al. (2006), in the present study TM4-ECPL is able to reproduce part of the outflow from the continents (Sinreich et al., 2007) and slight enhancement over the tropical oceans and the north Atlantic that are seen by SCIAMACHY. These patterns are under investigation and can not be properly reproduced by TM4-ECPL based on the processes that are actually considered to control CHOCHO levels in the model.'

With regard to potentially missing sources of glyoxal we have performed a new simulation (S4) with 7.3 Tg/y (4.8 biomass burning + 2.5 other combustion) of primary emissions - also following reviewer #2 suggestion. However, this simulation is not considered as the base case. Discussion and figures (1c, d, 2f and 3 k, l) are appropriately modified.

We agree with the reviewer that since satellite observations integrate the atmospheric column whereas surface observations refer to the lowest layer of the atmosphere, the comparison of model results to both of type of observations could provide insight to the location of a potentially missing source. However, as a result of the large uncertainties involved in the model calculations and the significant spatial and temporal variability of the observations conclusion on this point would be speculative. To investigate whether discrepancies over land are smaller or larger in industrial areas we also compared the model results with the SCIAMACHY columns over hot spot land areas. This comparison, which is included now in a new figure (1e), shows a good correlation between model results and observations. Discrepancy is smaller over industrial areas. Discus-

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sion in section 4.2 has been appropriately modified and reads as follows:

'Figure 1d focuses on the low resolution simulations S2, S3 and S4. Taking only the model results over the continents into consideration, the binned data, derived as explained, are plotted in Figure 1d against the annual mean vertical column of CHOCHO derived from SCIAMACHY. S3 considers all known photochemical sources of CHOCHO. S2 neglects the anthropogenic contribution to the secondary CHOCHO source. Finally, S4 accounts also for potential primary sources of CHOCHO from combustion. Figure 1d suggests that i) TM4-ECPL underestimates the annual mean CHOCHO columns observed by SCIAMACHY in 2005, ii) when accounting for the anthropogenic contribution to the photochemical formation of CHOCHO, TM4-ECPL results compare better with the observations and iii) consideration of primary anthropogenic sources of CHOCHO further improves the general agreement of model results with satellite observations over land.

Figure 1e focuses on 8 hot spot areas around the globe, including China where anthropogenic emissions increase rapidly (see figure caption for the geographic definition of the areas). It appears that i) simulation S3, considering only secondary sources of CHOCHO, agrees with satellite observations over these areas within the 95% confidence level, although generally it underestimates the columns over land (Figure 1d); ii) simulation S4 overestimates CHOCHO columns over source areas (Figure 1e), although it seems to perform relatively well (95% confidence level) with regard to the global burden of glyoxal over land (Figure 1d). Both simulations S3 and S4 underestimate the surface observations as shown in Table 2. Due to the high uncertainties both in potential primary emissions of CHOCHO and in satellite retrievals, these simulations are not conclusive with regard to the magnitude of the primary CHOCHO source. Overestimate of CHOCHO sink in the model could be responsible for part of the discrepancies between model results and observations.'

Moreover, earlier simulations performed with lower photolysis rates and by neglecting the wet removal of glyoxal have shown substantially higher glyoxal columns than the

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present base case simulation. However, both simulations were unrealistic and have not been retained for presentation in this manuscript. An additional test simulation with 2 orders of magnitude lower Henry law coefficient for glyoxal that is within the range of published values has been performed and results to about 8% reduction in the wet deposition removal and a 2% increase in the global tropospheric burden of glyoxal. This discussion is now included in the section 4.5.

We also provide a range in the anthropogenic contribution derived when considering primary emissions over land. Ocean emissions have not been included in the present study. 'Consideration of primary CHOCHO sources would further increase by about 20% the anthropogenic and by about 160% the biomass burning annual CHOCHO sources'.

We have also performed a test simulation by eliminating all anthropogenic emissions. This 'clean-air'; simulation with regard to glyoxal secondary sources is comparable to S2 (biogenic and biomass burning VOC emissions) allows the evaluation of the changes in oxidant levels to the glyoxal chemical formation. According to these calculations 52% of the glyoxal secondary production from biogenic and biomass burning VOC oxidation is due to the changes in oxidants levels due to anthropogenic activities.

This is now mentioned in section 4.5: 'TM4-ECPL also evaluates that the glyoxal secondary production from biogenic and biomass burning VOC oxidation has been significantly enhanced (almost doubled) due to the changes in oxidants levels induced from anthropogenic activities.'

References relevant to SOA formation from glyoxal have not been included in the present paper since this topic is not the focus of our modelling study.

Small English corrections have been taken into account.

Table 2 has been modified to report range of high and low resolution simulations (S3H and S3) as well as by adding simulations' low resolution simulation S4 (with primary emissions) seasonal mean values and standard deviation. Discrepancies can be partially due to the used of emission distributions for the year 2000 whereas the run is for 2005 (as explained in section 2.1). Overestimate by the model could be partially due to a missing sink of glyoxal related to particles as has already been mentioned in the ACPD paper in section 4.1.

We clearly state now in the discussion of Figure 1c that the high (S3-H) and the low (S3) resolution simulations behave similarly (no statistical difference) with regard to observations.

A table with the global annual emissions used in TM4-ECPL for the present study is now given in the Supplementary material (reference is made in section 2.1). The 33 Tg/y in POET correspond to the emissions of all aromatics lumped to toluene whereas the EDGAR inventory gives Tg of specific compounds (total 22 Tg/y).

Figure 1 has been modified and made homogeneous; see also replies to comments above. Some features showing anomalous high values of the glyoxal columns near a few ice/water borders are due to the gridding applied to the SCIA values in order to simulate the resolution of the model. The new Figures 1c and 1d with error bars facilitate comprehension of the binning of data. This consists in classifying in bin categories the all pairs of model and satellite data. The bin categories are defined based on the satellite data in intervals of 2.5E13 molecules cm-2 width and are shown in these figures as the average satellite value. This allows a classification of model results based on regularly increasing satellite data (independent from the location of the observation). The model values are deduced as the average (and std) of the model results corresponding to the satellite data in each bin category. Clarifications are now given in the text and the figure caption has been also improved. Precisely in the text it is mentioned that: 'To reduce the variability of the data, the modelled CHOCHO columns were grouped (binned) into values of 0.25E14 molecules cm-2 of SCIAMACHY observational data, independent from the exact location of these observations.'

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